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Experiments in polymer chemistry : the synthesis of fluoroaryloxy-dimethylsiloxane copolymers and the effects of radiation on methacrylic acid/acrylonitrile copolymers

Peter Anthony Fox
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DOI: <https://doi.org/10.31979/etd.sq72-ugrq>
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Fox, Peter Anthony, M.S.

San Jose State University, 1991

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Experiments in Polymer Chemistry:
The Synthesis of Fluoroaryloxy-dimethylsiloxane
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Methacrylic Acid/Acrylonitrile Copolymers

A Thesis
Presented to
The Faculty of the Department of Chemistry
San Jose State University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

By
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December, 1991

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Abstract

Experiments in Polymer Chemistry:

The Synthesis of Fluoroaryloxy-dimethylsiloxane Copolymers and the Effects of Radiation on Methacrylic Acid/Acrylonitrile Copolymers

by Peter A. Fox

This is a two part thesis exploring various aspects of polymer chemistry. Part one: The Synthesis of Poly(fluoroaryloxy-co-dimethylsiloxane) Polymers, concerns the synthetic schemes involved in the preparation of monomers and polymers of the above type. Monomers and polymers were characterized at each stage. Results and discussion covers various aspects of the synthetic scheme and analysis. Physical properties of the polymeric systems were also determined providing molecular weight, viscosity, and glass transition and decomposition temperatures.

Part two: The Effects of Radiation on Methacrylic Acid/ Acrylonitrile Copolymers. Copolymers of the above type were irradiated with ^{60}Co γ -rays under vacuum. Evaluation of the degradation mechanisms were studied utilizing electron spin resonance, yielding G[radical] for samples across the entire composition range at both 77 K and 303 K. The various radical species were also examined, and mechanisms for radical formation/ transformation were postulated. It appears that there is a synergistic effect causing an excessive radical yield when samples are irradiated at 77 K, and conversely, that these radical species are less stable than those of the homopolymer, and decay quickly at 303 K resulting in a lower amount of residual species. The radical species present seem to indicate that during the irradiation process, chain scission is a predominate in the polymer system.

This work is dedicated to my grandmother,

Katarina Hausser

who was my family's first scientist and
a person whose strength and perseverance
was a constant source of hope that with hard
work and patience, the impossible could be
achieved.

Acknowledgements

I wish to express my appreciation to my advisor Dr. R. Kellman, without whom none of this would have been possible. His guidance and occasional kick in the butt were invaluable during my course of study. I would like to thank the organic faculty of San Jose State University for their dedication to helping students such as myself. I would also like to thank Steve Ferla and FMC Corporation for assistance in obtaining polymer molecular weights by GPC. I must also show my appreciation to Dr. G. Selter for the mass spectral results. I am very grateful for the hospitality shown to me by Dr. D. J. T. Hill, Dr. P. Pomery, Prof. J. O'Donnell, and all the members of the Queensland polymer group during my stay at the University of Queensland in Australia.

I also would like to thank all my friends from Dr. Kellman's group who helped make my academic pursuits enjoyable as well as rewarding: Mark Krejchi, Sarifa Rejab, Peter Mahon, Sharish Shah, Kelli Kachel, Mark Nguyen, Carleen Odin, Sheryl Maraviov, and Sherita Maclamore. I wish express my thanks to Tri Li, Francine Kroeson, Seneke Perera, Mathew Celina, Peter Farrington, Trudy Carswell, Nigel St John, Heather Willis, Mary Austin, and Kayleen Campbell of the Queensland Polymer Group for making me welcome and for their friendship. I would also like to thank Steve Ferla for his friendship and encouragement as we pursued our academic goals.

I would also like to express my deepest thanks to my parents, James and Ludmilla Fox, who believed in me and were always there when I needed them most.

Table of Contents

Abstract.....	iii
Dedication.....	iv
Aknowledgements.....	v
Table of Contents.....	vi
List of Tables.....	vii
List of Figures.....	viii
List of Symbols and Abbreviations.....	xi
Part 1: Synthesis of Poly(fluoroaryloxy-co-dimethylsiloxane) Polymers	
Introduction.....	1
Background.....	4
Experimental.....	10
Results and Discussion.....	23
Conclusions.....	37
Part 2: The Effects of Radiation on Methacrylic Acid/Acrylonitrile Copolymers	
Introduction.....	53
Background.....	54
Experimental.....	59
Results and Discussion.....	67
Conclusions.....	76
Appendix A: Fricke Dosimetry.....	104
References.....	107

List of Tables

Table 1.1: Differential Scanning Calorimetry and Thermal Gravimetric.....	38
Analysis of Monomers and Copolymers	
Table 1.2: GPC and Viscosity Analysis.....	38
Table 2.1: Techniques used to Determine G[values] for Polymers.....	55
Table 2.2: Reaction Conditions and Yields for the Preparation of.....	78
Methacrylic Acid/Acrylonitrile Copolymers	
Table 2.3: Distribution of Triad Fractions in Methacrylic Acid/.....	78
Acrylonitrile Copolymers	

List of Figures

1.1	Kinetic Plot of the Reaction of Decafluorobiphenyl with.....	39
	4-Methoxyphenol in Acetone at 56°C	
1.2	Kinetic Plot of the Reaction of Decafluorobiphenyl with.....	40
	4-Methoxyphenol in Acetone at 25°C	
1.3	Mass Spectrum of the Product formed by the Reaction of.....	41
	4-isopropylphenol with 1,3-bis(diethylamino)tetramethyldisiloxane	
1.4	Mass Spectrum of the Byproduct formed in the Reaction of.....	42
	4-isopropylphenol with 1,3-bis(diethylamino)tetramethyldisiloxane	
1.5	75MHz ¹³ C Spectra of Poly(B4HPB-co-DS).....	43
1.6	75MHz ¹³ C Spectra of Poly(B3HPB-co-DS).....	44
1.7	75MHz ¹³ C Spectra of Poly(B4HPB-co-PS).....	45
1.8	300MHz ¹ H Spectra of Poly(B4HPB-co-DS).....	46
1.9	300MHz ¹ H Spectra of Poly(B3HPB-co-DS).....	47
1.10	300MHz ¹ H Spectra of Poly(B4HPB-co-PS).....	48
1.11	282MHz ¹⁹ F Spectra of Poly(B4HPB-co-DS).....	49
1.12	282MHz ¹⁹ F Spectra of Poly(B3HPB-co-DS).....	50
1.13	282MHz ¹⁹ F Spectra of Poly(B4HPB-co-PS).....	51
1.14	Ultra-Violet/Visible Spectrum of Poly(B4HPB-co-PS).....	52
2.1	¹³ C NMR Spectra Showing the Carbonyl and Nitrile Peaks of.....	79
	Methacrylic Acid/Acrylonitrile Copolymers	
2.2	The Effect of γ-rays on the ESR Spectrum of Polyacrylonitrile.....	80

2.3	The Effect of γ -rays on the ESR Spectrum of 11% Methacrylic.....81 Acid/89% Acrylonitrile Copolymer
2.4	The Effect of γ -rays on the ESR Spectrum of 24% Methacrylic.....82 Acid/76% Acrylonitrile Copolymer
2.5	The Effect of γ -rays on the ESR Spectrum of 36% Methacrylic.....83 Acid/64% Acrylonitrile Copolymer
2.6	The Effect of γ -rays on the ESR Spectrum of 44% Methacrylic.....84 Acid/56% Acrylonitrile Copolymer
2.7	The Effect of γ -rays on the ESR Spectrum of 63% Methacrylic.....85 Acid/37% Acrylonitrile Copolymer
2.8	The Effect of γ -rays on the ESR Spectrum of 75% Methacrylic.....86 Acid/25% Acrylonitrile Copolymer
2.9	The Effect of γ -rays on the ESR Spectrum of 89% Methacrylic.....87 Acid/11% Acrylonitrile Copolymer
2.10	The Effect of γ -rays on the ESR Spectrum of 91% Methacrylic.....88 Acid/9% Acrylonitrile Copolymer
2.11	The Effect of γ -rays on the ESR Spectrum of Polymethacrylic Acid.....89
2.12	Effect of Composition on G[radical] in Methacrylic Acid/Acrylonitrile.....90 Copolymers
2.13	Simulated ESR Spectra of Radical Species Found in Irradiated.....91 Polyacrylonitrile and Polymethacrylic Acid
2.14	Difference ESR Spectra of Methacrylic Acid/Acrylonitrile.....92 Copolymers Irradiated at 77 K
2.15	Difference ESR Spectra of Methacrylic Acid/Acrylonitrile.....93 Copolymers Irradiated at 303 K
2.16	Effect of Composition on the Glass Transition Temperature of.....94 Methacrylic Acid/Acrylonitrile Copolymers
2.17	Effect of Temperature on the Radical Yield in Methacrylic Acid/.....95 Acrylonitrile Copolymers

2.19	Effect of Temperature on the ESR Spectrum of 44% Methacrylic.....97 Acid/56% Acrylonitrile Irradiated at 77 K
2.20	Effect of Temperature on the ESR Spectrum of 75% Methacrylic.....98 Acid/25% Acrylonitrile Irradiated at 77 K
2.21	Difference ESR Spectra from the Warmup of 24% Methacrylic.....99 Acid/76% Acrylonitrile Copolymer from 110 K to 330 K
2.22	Difference ESR Spectra from the Warmup of 44% Methacrylic.....100 Acid/56% Acrylonitrile Copolymer from 110 K to 330 K
2.23	Difference ESR Spectra from the Warmup of 75% Methacrylic.....101 Acid/25% Acrylonitrile Copolymer from 110 K to 330 K
2.24	Difference ESR Spectra from the Photobleaching of.....102 44% Methacrylic Acid/56% Acrylonitrile Irradiated at 77 K
2.25	Difference ESR Spectra from the Photobleaching of.....103 63% Methacrylic Acid/37% Acrylonitrile Irradiated at 77 K
A.1	Concentration of Iron(III) in Fricke Solution with Length of Exposure.....106 to 1.25MeV γ -Rays

List of Symbols and Abbreviations

AN	Acrylonitrile
B3HPB	Bis-4,4'-(3-hydroxyphenyloxy)octafluorobiphenyl
B4HPB	Bis-4,4'-(4-hydroxyphenyloxy)octafluorobiphenyl
DS	Tetramethyldisiloxane
DSC	Differential Scanning Calorimetry
ESR	Electron Spin Resonance
F_{AMA}	fraction of a particular triad sequence of units along the backbone of a polymer chain.
GPC	Gel Permeation Chromatography
ΔH_m	Heat of Melting
$[\eta]$	Intrinsic viscosity
η_{inh}	Inherent viscosity
MAA	Methacrylic acid
PAN	Polyacrylonitrile
PMAA	Polymethacrylic acid
PS	Decamethylpentasiloxane
SLPTC	Solid Liquid Phase Transfer Catalysis
T_c	Crystallization Temperature
T_g	Glass Transition Temperature
T_m	Melting Temperature

Part 1: Synthesis of Poly(fluoroaryloxy-co-dimethylsiloxane) Polymers

Introduction

As technical advancement proceeds, the need for new materials increases. The role of synthetic polymers in materials science and engineering has become crucial. Copolymer synthesis provides a versatile way of preparing a material to meet a specific application. Since some properties like thermal stability and chemical resistance are inherent to the molecular architecture of the polymer, the structure of the copolymer can be designed with these factors in mind. Certain copolymers exhibit physical properties between those of the homopolymers from which they were derived. By combining two materials with very different physical properties we will obtain a series of copolymers with a large variation in physical properties. For this study we chose to synthesize and study copolymers of polydimethylsiloxane and fluoroaryl ethers.

Siloxanes find many important applications in biomedical implants and other devices. Siloxanes have been tested for use as contact lenses, as they have excellent clarity, flexibility, and gas permeability. Pure polydimethylsiloxane without fillers can pass oxygen at a rate of $367 \times 10^{13} \text{ cm}^3 (298 \text{ K}, 1 \text{ bar}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$.¹ This is far superior to some of the older polymers used in the making of contact lenses such as poly(methyl-methacrylate), which has an oxygen permeability of $0.116 \times 10^{13} \text{ cm}^3 (298 \text{ K}, 1 \text{ bar}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$.¹ Siloxanes are also used in slow release drug implants, cosmetic alteration, and cartilage replacement because of their biocompatibility.² One of the major drawbacks of siloxanes are their poor resistance to creep (cold flow). This is prevented in current processing techniques by crosslinking the polymer with a chemical crosslinking agent.

Although creep is arrested, the byproducts of the crosslinking reaction are trapped within the polymer matrix. This can be a problem especially in biomedical applications. These crosslinking agents can leech out of the rubber and into the surrounding tissues. These crosslinking agents can also interfere with slow release drug implants by reacting with the drug and inhibiting diffusion. The siloxane is also locked into the shape the material was in when it was crosslinked. Thus there is no way of refabricating these materials after they have exceeded their usefulness in a specific form.

Fluoropolymers are also found in biomedical devices. Polytetrafluoroethylene, PTFE, is used for sutures, arterial prostheses, tissue reinforcement, and in other biomedical applications.³ Its unique surface properties and chemical resistance have caused it to come under scrutiny for a variety of other medical devices and replacement prosthetics. Considerable investigation of fluoroelastomers has led to a variety of polymers for use as thermally resistant elastomers. Unfortunately, most of the elastomers made from perfluoroethylene and hexafluoropropylene have T_g 's of -20°C at the lowest.⁴ Fluorosilicones although excellent elastomers having T_g 's about -60°C , fail to exhibit the thermal stability of PTFE.⁴

It is known that aromatic ring systems have a high tendency towards the formation of crystalline solids. If one can synthesize a copolymer which contains crystalline regions of fluoroaryl ether segments and flexible amorphous regions of siloxane segments, the resulting copolymer should have the flexibility of polydimethylsiloxane but be resistant to creep. However, because these crystalline regions can be melted, melt processing and refabrication become feasible. Such materials are known as thermoplastic elastomers. Since no crosslinking agents have been added, these materials are also can be produced free of impurities, making them suitable for biomedical applications. Furthermore, since it is also possible to manipulate the amounts of the two types of monomer units in the copolymer, we should

also be able to tailor its physical properties. For example, the glass transition temperature [T_g] is the temperature above which the amorphous regions of the polymer matrix 'melt' and the material becomes rubbery. The T_g of a copolymer will be somewhere between that of the two parent polymers. Polydimethylsiloxane has a T_g of -147°C ,⁵ and poly(resorsinol-co-decafluorobiphenyl) has a T_g of 126°C .⁶ This means that we can manipulate the mole fractions of the two monomer types and obtain a series of copolymers with T_g s within this 273°C range. Other properties such as the melting point T_m and gas permeability can be modified as well. By combining the thermal and chemical stability of fluoroaryl ether polymers with thermal stability of siloxanes, we hope to achieve the synthesis of a series of polymers with a wide range of possible uses.

Background

Condensation polymerization techniques have been used to achieve the synthesis of the high molecular weight segmented copolymers. Condensation polymerization occurs by a step-growth mechanism whereby molecular weight is determined by the equations shown below. As the reaction proceeds longer and longer chains are formed. These are controlled solely by the percent conversion and stoichiometric balance. The kinetic factors determining the chain length are governed by the equation:⁷

$$\overline{DP}_n = \frac{1+r}{1+r-2rp} \quad [1.1]$$

$\overline{DP}_n$ = the average length of the polymer chain

$r = N_a/N_b$ (where N_a = the # of functional groups of the a type,

N_b = the # of functional groups of the b type, and $N_a \leq N_b$)

p = the percent conversion or extent of reaction

There is much implied by the above equation. Generally, the optimal mechanical properties of a polymer are exhibited when high molecular weight or $\overline{DP}_n$, in most cases when $\overline{DP}_n \geq 100$ is achieved. To do this, the values of r and p must both be approximately or equal to one. Problems in achieving high molecular weight are encountered when r and p deviate from these values. If we use an exact molar equivalent of monomer 1 to that of monomer 2 (i.e. $N_a = N_b$), then the equation 1.1 simplifies as follows:⁷

$$\overline{DP}_n = \frac{1}{1-p} \quad [1.2]$$

Thus as p approaches 1 or quantitative conversion, $\overline{DP}_n$ approaches infinity. Therefore, high molecular weight material will not be obtained until late in the reaction (eg. if $p = 0.99$, $\overline{DP}_n = 100$). Conversely, if we let the reaction go to

completion (ie. $p = 1$), then equation 1.1 simplifies:⁷

$$\overline{DP}_n = \frac{1+r}{1-r} \quad [1.3]$$

Thus as r approaches 1, $\overline{DP}_n$ approaches infinity. Therefore, high molecular weight material will not be obtained unless an exact stoichiometric balance of the two monomers is obtained (eg. if monomer 1 is only 98% pure, $r = 0.98$, and $\overline{DP}_n = 100$). Thus the reaction must go to completion and the monomers must be pure to achieve high molecular weight polymers.

The physical properties of the copolymers are very dependent upon the copolymer microstructure. If we polymerize short segments of fluoroaryl ether oligomer(s) with reactive short dimethylsiloxane oligomers, we will get the alternating microstructure as indicated below:

Thus we will get copolymers with an average of physical properties between those of the respective homopolymers. For example, a polymer with the above composition would be expected to have a T_g approximately midway between those of the homopolymers will be observed. As we increase the length of the siloxane unit we will get the more block-like microstructure indicated below:

The T_g of this copolymer will be closer to that of pure polydimethylsiloxane and the material would be more rubbery. Assuming that crystallization of the fluoroaryl ether segments can occur, physical crosslinks will be established. By using higher molecular weight fluoroaryl ether components into the backbone we get the block-like microstructure shown below:

-A-A-A-S-A-A-A-S-A-A-A-S-A-A-A-S-A-A-A-S-A-A-A-S-A-A-A-S-A-A-A-S-

The above material will be more glass-like (plastic), but more impact resistant than that of the fluoroaryl ether homopolymer due to the energy absorbing flexible siloxane units. To promote the formation of crystalline regions in the copolymer matrix, it may be necessary to synthesize block type copolymers with large segments of both types of units along the chain as shown below:

-A-A-A-S-S-S-S-S-A-A-A-S-S-S-S-A-A-A-S-S-S-S-A-A-A-S-S-S-S-

The synthesis of a number of copolymers will be required to establish the physical behavior of the polymers in relation to their microstructures.

Experimental

Acetone was dried over CaSO_4 , decanted, refluxed over P_2O_5 , and distilled under dry nitrogen. The water content was determined using a Mettome Coulometric Karl Fischer titrator operating at -10°C (to prevent ketal formation and thus an erroneous response due to elimination of water)⁸ and was determined to be 0.096 mmol $\text{H}_2\text{O}/\text{ml}$ acetone. The acetone was degassed by the freeze/thaw method before use. 1,4,7,10,13,16-Hexaoxaoctadecane [18-Crown-6] (Aldrich) was recrystallized from its acetonitrile complex.⁹ Decafluorobiphenyl (Aldrich) was recrystallized from benzene. 4-Methoxyphenol (Aldrich) was recrystallized from toluene. 3-Methoxyphenol (Aldrich) was used as received. Anhydrous potassium carbonate was ground and oven dried at 150°C overnight. Methylene chloride was extracted with conc. H_2SO_4 , water, saturated NaHCO_3 , then stirred over CaSO_4 , filtered, refluxed over P_2O_5 , and distilled. The 0.5 M boron tribromide solution was prepared by combining 200 mL of dry CH_2Cl_2 with 25 g of BBr_3 (Aldrich). The solution stored in a brown sure-seal bottle under a dry nitrogen blanket. 1,3-Dichloro-1,1,3,3-tetramethyldisiloxane (Petrarch) was distilled before use under a dry nitrogen blanket and the fraction coming over at 138°C collected. Tetrahydrofuran was dried over KOH pellets, distilled, refluxed over sodium with added benzophenone until the characteristic blue color appeared, and then distilled. 1,9-bis(dimethylamino)decamethylpentasiloxane was obtained by fractional distillation of dimethylamino-endcapped siloxane oligomers (Petrarch) at 0.6 mmHg and the fraction boiling at 119°C collected. Diethylamine (Kodak) was distilled from KOH at 54.5°C . 4-Isopropylphenol was recrystallized from hexane. Toluene was refluxed over sodium and then distilled. Bisphenol-A was recrystallized from toluene.

Characterization of the copolymers was achieved by a variety of methods. Using a Brüker 300 MSL ^1H , ^{13}C , and ^{19}F NMR spectra were

obtained for most monomers and copolymers at spectral frequencies of 300.13, 282.4, and 75.5 MHz respectively. Some ^1H NMR spectra were obtained on a Varian T-60 60MHz NMR, and a IBM NR80 80MHz FTNMR. Elemental analysis was performed by Midwest Microlabs. Melting points, crystallization temperatures (T_c), and glass transition temperatures were determined using a Perkin Elmer DSC7 utilizing approximately 5 mg of sample in an aluminum pan ramped over an appropriate range at a rate of $10^\circ\text{C}/\text{min}$. Nitrogen was used as an inert atmosphere. Decomposition temperatures [T_d] were determined by employing a Perkin Elmer TGA2 ramped at a rate of $10^\circ\text{C}/\text{min}$ under an argon atmosphere and the T_d reported as the temperature indicating 10% weight loss. HPLC was conducted on samples using a Hewlett Packard 1050 HPLC equipped with a UV/Vis multiwavelength detector set at 254 nm, and a Waters C18 column. In all cases an 80% acetonitrile/20% water mobile phase was used. Mass spectral analysis was carried out on a Finnigan 1020 quadropole GCMS utilizing an electron beam ion source of 70 eV. This was done using an oven temperature of 260°C through a 30 m capillary column coated with DB5. Gel Permeation Chromatography was determined using a Waters GPC system equipped with ultrastyrigel columns, UV and refractive index detectors, and a computerized data analysis system. THF was the eluting solvent, and the system calibrated with narrow molecular weight styrene standards and the molecular weight performed by using a universal calibration standard calculation. Viscosity measurements were determined with an Ubbelöhde viscometers and chloroform as the solvent at 30°C . A solution of 0.075 g of polymer was dissolved in 10 mL of chloroform, and the inherent viscosity η_{inh} determined using equation 1.4:¹⁰

$$\eta_{\text{inh}} = \frac{\ln(t/t_0)}{c} \quad [1.4]$$

$$[\eta] = [\eta]_{\text{inh} \rightarrow 0} \quad [1.5]$$

t = flow time for polymer solution

t_0 = flow time for chloroform alone

Dilution with more chloroform was used to obtain inherent viscosities at two other concentrations. Extrapolation to zero concentration gave the intrinsic viscosity $[\eta]$. The results of GPC and viscosity analyses are reported in Table 1.3. Ultra-violet/visible spectroscopy on these materials was determined for selected samples using a HP 8451A diode array spectrophotometer. This was done in a solution of chloroform. Infrared spectroscopy was conducted utilizing a Perkin Elmer 1800 FTIR interfaced to a Perkin Elmer 7500 computer. Transmission spectra for mid-IR range of 4000-450 cm^{-1} were obtained from films or KBr pellets.

Preparation of 4,4'-bis(4-methoxyphenyloxy)octafluorobiphenyl

Decafluorobiphenyl 6.16 g (18.44 mmol), 18-crown-6 2.97g (11.23 mmol), and K_2CO_3 16.86 g (121.68 mmol) were combined in a 100 mL round bottom three neck flask with a magnetic stirbar. Then 70 mL of acetone containing 25.82 mmol of water was added. 4-Methoxyphenol 5.02 g (40.6 mmol) was then added. The flask was equipped with a condenser, and flushed with dry nitrogen. The reaction mixture was heated to reflux with stirring. During the course of the reaction, aliquots were taken for HPLC analysis with a capillary tube, and the sample transferred into a vial containing 1 mL of acetonitrile. After ca. 1 hour, the reaction mixture was poured into a separatory funnel, combined with 50 mL of ethyl ether, and washed with 50 mL of water. The aqueous phase was removed, and the organic layer washed with 50 mL of dilute HCl and then 50 mL of saturated NaCl. The ether solution was then dried ($MgSO_4$), and rotary evaporated to give 9.93 g (99%) of a white solid. The product was recrystallized from petroleum ether to give white plates, mp = 91.3°C.

Anal. calcd. for $C_{26}H_{14}F_8O_4$: C, 57.57%; H, 2.60%; F, 28.02%.

Found: C, 57.65%; H, 2.33%; F, 24.73%

1H NMR: ($CDCl_3$) δ 7.02, 6.72 (A_2B_2 , 8H, Ar-H), 3.78 (s, 6H, O- CH_3)

^{19}F NMR: ($CDCl_3$ w/ $CFCl_3$ int. std.) δ -138.82 (q, 4F, Ar-F), -154.03

(A_2B_2 , 4F, Ar-F)

^{13}C NMR: ($CDCl_3$) δ 156.2, 151.0 (s, C_{Ar-O}), 145.03, 141.63 (A_2B_2 , C_{Ar-F}),

135.3 (s, C_{ArF-O}), 117.32, 114.82 (s, C_{Ar-H}), 102.6 ($C_{ArF-C_{ArF}}$), 55.70

(s, O- CH_3)

Preparation of 4,4'-bis(3-methoxyphenoxy)octafluorobiphenyl

Decafluorobiphenyl 6.16 g (18.44 mmol), 18-crown-6 2.97 g (11.23 mmol), and K_2CO_3 16.86 g (121.68 mmol) were combined together in 140 mL of acetone containing 25.82 mmol of water in a 100 mL round bottom three neck flask with a magnetic stirbar. 3-Methoxyphenol 4.15 mL (37.8 mmol) was then added. The flask was equipped with a condenser, and flushed with dry nitrogen. The reaction mixture heated to reflux with stirring. During the course of the reaction, aliquots were taken for HPLC analysis with a capillary tube, and the sample transferred into a vial containing 1 mL of acetonitrile. After ca. 1 hour, the reaction mixture was poured into a separatory funnel, combined with 50 mL of ethyl ether, and washed with 50 mL of water. The aqueous phase was removed, and the organic layer washed with 50 mL of dilute HCl and then 50 mL of saturated NaCl. The ether solution was then dried ($MgSO_4$), and rotary evaporated to give 7.94 g (79%) of a white solid. The product was recrystallized from petroleum ether to give white plates, mp = 88.4°C.

Anal. calc. for $C_{26}H_{14}F_8O_4$: C, 57.57%; H, 2.60%; F, 28.02%.

Found: C, 57.76%; H, 2.52%; F, 28.40%

IR (KBr pellet): 3067, 2649, 1603, 1587, 1476, 1437, 1187, 1174, 1148, 1091, 1076, 1048, 999, 978, 905, 873, 850, and 762 cm^{-1}

1H NMR: ($CDCl_3$) δ 7.25 (t, 2H, Ar-H), 6.69 (d, 2H, Ar-H), (s, 2H, Ar-H), 3.78 (s, 6H, CH_3 -O)

^{19}F NMR: ($CDCl_3$ w/ $CFCl_3$ int. std.) δ -138.47 (q, 4F, Ar-F), -154.00

(A_2B_2 , 4F, Ar-F)

^{13}C NMR: ($CDCl_3$) δ 161.0, 158.0 (s, C_{Ar} -O), 145.0, 141.7 (A_2B_2 , C_{Ar} -F), 135.3 (s, C_{ArF} -O), 130.3, 109.4, 107.7 (s, C_{Ar} -H), 102.6 (s, C_{ArF} - C_{ArF}), 55.5 (s, CH_3 -O)

Preparation 4-(4-methoxyphenoxy)nonafluorobiphenyl

Decafluorobiphenyl 6.16 g (18.44 mmol), K_2CO_3 3.82 g (27.66 mmol), and 18-crown-6 1.34 g (5.10 mmol) were combined with 70 mL of acetone. Finally, 4-methoxyphenol 2.29 g (18.44 mmol) was added to the solution, and the mixture was refluxed for an hour with stirring. The reaction mixture was transferred into a separatory funnel after cooling, combined with 50 mL of ethyl ether, and washed with 50 mL of water. The aqueous phase was removed, and the organic layer washed with dilute HCl and saturated NaCl. The ether solution was then dried ($MgSO_4$), and rotovapped to give 7.94 g (99%) of a white solid. This was recrystallized from 80% petroleum ether/20% toluene, mp = 129.9°C.

Anal. calcd. for $C_{19}H_7F_9O_2$: C, 52.05%; H, 1.60%; F, 39.04%.

Found: C, 52.07%; H, 1.61%; F, 38.94%

^{19}F NMR: ($CDCl_3$ w/ $CFCl_3$ int. std.) δ -137, -138.8 (d, 2F, Ar-F),
150.8 (t, 1F, Ar-F), -153.8, -161.0 (t, 2F, Ar-F)

Preparation of 4,4'-bis(4-hydroxyphenyloxy)octafluorobiphenyl

4,4'-bis(4-methoxyphenyloxy)octafluorobiphenyl 1.00 g (1.84 mmol) of was added to a 10 mL round bottom single neck reaction flask. The flask was fitted to an air condenser, and flushed with dry nitrogen. The flask was cooled to -78°C using a dry ice/isopropanol bath. Then 7.36 mL of a 0.5 M solution of BBr_3 in CH_2Cl_2 (3.86 mmol), was added through the condenser, and the nitrogen blanket replaced. The reaction mixture was protected from light. After 19 hours the mixture was poured into water and extracted with ethyl ether. The aqueous phase was removed, and the organic layer extracted with 5% NaOH . The organic layer was then discarded, and the aqueous phase neutralized with HCl . The reaction mixture was extracted with ethyl ether again, and the aqueous phase discarded. The organic layer was dried (MgSO_4), filtered, and rotovapped yielding 0.941 g (91%) of a white solid. This was recrystallized from methanol/water to give small iridescent needles. mp. = 209.8

Anal. calcd. for $\text{C}_{24}\text{H}_{10}\text{F}_8\text{O}_4$: C, 56.04%; H, 1.95%; F, 29.55%.

Found: C, 56.06%; H, 1.72%; F, 30.41%

IR (KBr pellet): 3423, 3068, 2332, 1234, 1506, 1491, 1476, 1451, 1420, 1251, 1239, 1197, 1156, 1096, 1077, 995, 984, 956, 837, and 830 cm^{-1}

^1H NMR: (Acetone- D_6) δ 8.35 (s, 2H, O-H), 7.01, 6.89 (A_2B_2 , 8H, Ar-H)

^{19}F NMR: (Acetone- D_6 w/ CFCl_3 int. std.) δ -139.2 (q, 4F, Ar-F), -154.72

(A_2B_2 , 4F, Ar-F)

^{13}C NMR: (Acetone- D_6) δ (s, $\text{C}_{\text{Ar-O}}$), 145.03, 141.63 (A_2B_2 , $\text{C}_{\text{Ar-F}}$), 135.3 (s, $\text{C}_{\text{ArF-O}}$), 117.32, 114.82 (s, $\text{C}_{\text{Ar-H}}$), 102.6 ($\text{C}_{\text{ArF-C}_{\text{ArF}}}$)

Preparation of 4,4'-bis(3-hydroxyphenyloxy)octafluorobiphenyl

4,4'-bis(3-methoxyphenyloxy)octafluorobiphenyl 5.00 g (9.22 mmol) of was added to a 10 mL round bottom single neck reaction flask. The flask was fitted to an air condenser, and flushed with dry nitrogen. The flask was cooled to -78°C using a dry ice/isopropanol bath. Then 24.5 mL of a 0.5 M solution of BBr₃ in CH₂Cl₂ (12.3 mmol), was added through the condenser, and the nitrogen blanket replaced. The reaction mixture was protected from light. After 19 hours the mixture was poured into water and extracted with ethyl ether. The aqueous phase was removed, and the organic layer extracted with 5% NaOH. The organic layer was then discarded, and the aqueous phase neutralized with HCl. The reaction mixture was extracted with ethyl ether again, and the aqueous phase discarded. The organic layer was dried (MgSO₄), filtered, and rotovapped yielding a white solid. This was recrystallized from ethanol/water yielding 3.291g (69%). mp. = 106.9°C

Anal. calcd. for C₂₄H₁₀F₈O₄: C, 56.04%; H, 1.95%; F, 29.55%.

Found: C, 54.46%; H, 2.27%; F, 29.35%

¹H NMR: (Acetone-D₆) δ 8.35 (s, 2H, O-H) , 7.36 (t, 2H, Ar-H), 6.80, 6.75 (dd, 2H, Ar-H) 6.79 (s, 2H, Ar-H)

¹⁹F NMR: (Acetone-D₆ w/ CFCl₃ int. std.) δ -138.8 (q, 4F, Ar-F), -154.2 (A₂B₂, 4F, Ar-F)

¹³C NMR: (Acetone-D₆) δ 159.3, 158.0 (s, C_{Ar}-O), 145.3, 141.8 (dd, C_{ArF}-F), 135.4 (t, C_{ArF}-O), 130.76, 111.4, 106.5, 103.3 (s, C_{Ar}-H), 102.6 (t, C_{ArF}-C_{ArF})

Preparation of 1,3-bis(diethylamino)-1,1,3,3-tetramethyldisiloxane¹¹

45 mL of 1.11M (determined by NMR¹²) n-butyl lithium in hexane (50 mmol), and an equal volume of ether were combined in the reaction vessel which had been cooled to -78°C with a blanket of dry nitrogen. Diethylamine 7.8 mL (75 mmol) was syringed into the cooled reaction flask through a septum. The flask was fitted with an addition funnel containing 4.9 mL (25 mmol) 1,3-dichloro-1,1,3,3-tetramethyldisiloxane, which was added dropwise. The reaction mixture was allowed to warm up to room temperature. The solvents were distilled off at atmospheric pressure, and the product isolated by vacuum distillation. This was distilled a second time at 2.5 mmHg and the fraction boiling at 60-65°C collected yielding 3.53 g (51%). Density: 0.91 g/mL

60 MHz ¹H NMR (CDCl₃) 2.90 (q, 8H, CH₂R-N), 1.05 (t, 12H, CH₃-CH₂), 0.15 (s, 12H, CH₃-Si)

Preparation of 1,3-bis(dimethylamino)-1,1,3,3-tetramethyldisiloxane¹³

100 mL of 1.6M n-butyl lithium in hexane (160 mmol), and 100 mL of anhydrous ethyl ether were combined in the reaction vessel which had been cooled to -78°C with a blanket of dry nitrogen. Dimethylamine 15.9 mL (200mmol) was canulated into a sealed, cooled graduated cylinder, and the contents of the cylinder allowed to warm up to room temperature and distill into the cooled reaction flask. When all of the contents had been added, the flask was fitted with an addition funnel containing 15.7 mL (80mmol) 1,3-dichloro-1,1,3,3-tetramethyldisiloxane and the siloxane added over a 30 minute period. The reaction mixture was then allowed to warm up to room temperature. The solution was tranfered to a single neck flask, and the solvents were distilled at atmospheric pressure. The product isolated by vacuum distillation. This was distilled a second time at atmospheric pressure and the fraction boiling at 178-181°C collected yielding 11.12 g (61%). Density: 0.87 g/mL

80 MHz ¹H NMR (CDCl₃) 2.49 (s, 12H, CH₃-N), 0.06 (s, 12H, CH₃-Si)

Preparation of 1,3-bis(4-isopropylphenoxy)tetramethyldisiloxane

4-isopropylphenol 0.4513 g (3.324 mmol) was combined with 5 mL of toluene in a silated reaction flask. 1,3-bis(diethylamino)-1,1,3,3-tetramethyldisiloxane 0.4483 g (1.620 mmol) was combined with 5 mL of toluene in a silated addition funnel. The system was fitted with a condenser, a magnetic stirbar, and a tube to flush dry argon through the solvent. The reaction flask was heated to reflux in an oil bath, and the 1,3-bis(diethylamino)-1,1,3,3-tetramethyldisiloxane solution added dropwise over a 15 minute period. The reaction was continued for another 9.25 hours, transferred to a single neck flask, and the toluene removed by rotary evaporation. A yellow tinted liquid, 0.6274 g (96%), was obtained. HPLC analysis showed the material to be 97% of the desired product. MS molecular ion: 402 m/e; base peak: 186 m/e.

80 MHz ^1H NMR

(CDCl_3) 7.15, 6.72 (A2B2, 8H, Ar-H), 2.86 (sept., 2H, CHR2), 1.21 (d, 12H, $\text{CH}_3\text{-R}$), 0.23 (s, 12H, $\text{CH}_3\text{-Si}$)

Preparation of Poly(4,4'-(isopropylidene)biphenol-co-tetramethyldisiloxane) from 1,3-bis(diethylamino)-1,1,3,3-tetramethyldisiloxane

Bisphenol-A 0.3570 g (1.564 mmol) was combined with 5 mL of toluene in a silitated reaction flask. 1,3-bis(diethylamino)-1,1,3,3-tetramethyldisiloxane 0.4541 g (1.642 mmol) was combined with 5 mL of toluene in a silitated addition funnel. The system was fitted with a condenser, a magnetic stirbar, and a tube to flush dry argon through the solvent. The reaction flask was heated to reflux in an oil bath, and the 1,3-bis(diethylamino)-1,1,3,3-tetramethyldisiloxane solution added dropwise over a 15 minute period. The mixture was poured into isopropanol after an hour. The clear viscous liquid was collected by rotary evaporation dried overnight in the vacuum oven. $\eta_{inh} = 0.191$ (0.75g/dL). DSC: $T_g = -4.8^\circ\text{C}$.

80 MHz ^1H NMR: (CDCl_3) δ 7.07, 6.25 (A_2B_2 , 8H, Ar-H), 1.62 (s, 6H, $\text{CH}_3\text{-C}$), 0.21 (s, 12H, Si- CH_3)

Preparation of Poly(4,4'-(isopropylidene)biphenol-co-tetramethyldisiloxane) from 1,3-bis(dimethylamino)-1,1,3,3-tetramethyldisiloxane

Bisphenol-A 0.4388 g (1.922 mmol) was combined with 5 mL of toluene in a silated reaction flask. 1,3-bis(dimethylamino)-1,1,3,3-tetramethyldisiloxane 0.4561 g (2.023 mmol/500 μ l) was combined with 5 mL of toluene in an silated addition funnel. The system was fitted with a condenser, a magnetic stirbar, and a tube to flush dry argon through the solvent. The reaction flask was heated to reflux in an oil bath, and the 1,3-bis(dimethylamino)-1,1,3,3-tetramethyldisiloxane solution added dropwise over a 15 minute period. The mixture was poured into isopropanol after an hour. The clear viscous liquid was collected by rotary evaporation and dried overnight in the vacuum oven. η_{inh} = 0.56 (0.76g/dL). DSC: T_g = -4.8°C.

80 MHz ^1H NMR: (CDCl_3) δ 7.07, 6.25 (A_2B_2 , 8H, Ar-H), 1.62 (s, 6H, $\text{CH}_3\text{-C}$), 0.21 (s, 12H, Si- CH_3)

Preparation of Poly(4,4'-bis(4-oxyphenyloxy)octafluorobiphenyl-co-tetramethyldisiloxane)

4,4'-bis(4-hydroxyphenyloxy)octafluorobiphenyl 2.0974 g (1.0387 mmol) was combined with 5 mL of toluene in a silated reaction flask. 1,3-bis(dimethylamino)- 1,1,3,3-tetramethyldisiloxane 0.4486 g (2.0348 mmol) was combined with 5 mL of toluene in a silated addition funnel. The system was fitted with a condenser, a magnetic stirbar, and a tube to flush dry argon through the solvent. The reaction flask was heated to reflux in an oil bath, and the 1,3-bis(dimethylamino)- 1,1,3,3-tetramethyldisiloxane solution added dropwise over a 15 minute period. The mixture was poured into isopropanol after an hour. The white solid was collected by filtration and dried overnight in the vacuum oven. Yield 1.235 g (94.2%). DSC: $T_g = 37.9^\circ\text{C}$. TGA: $T_d = 490^\circ\text{C}$. $[\eta] = 0.445$. GPC: $M_n = 56087$, $M_w = 111030$.

Anal. calcd. for $\text{C}_{28}\text{H}_{20}\text{F}_8\text{O}_5\text{Si}_2$: C, 52.17%; H, 3.12%; F, 23.57%.

Found: C, 51.83%; H, 2.74%; F, 23.96%

IR (film): 3050, 2950, 1651, 1603, 1492, 1268, 1196, 1077, 1006, 985, 931, 841, 814, and 727 cm^{-1}

^1H NMR: (CDCl_3) δ 6.95, 6.85 (A_2B_2 , 8H, Ar-H), 0.24 (s, 12H, Si- CH_3)

^{19}F NMR: (CDCl_3 w/ CFCl_3 int. std.) δ -138.9 (q, 4F, Ar-F), -154.0 (A_2B_2 , 4F, Ar-F)

^{13}C NMR: (CDCl_3) δ 151.7, 150.7 (s, $\text{C}_{\text{Ar-O}}$), 145.0, 141.63 (dd, $\text{C}_{\text{Ar-F}}$),

135.3 (s, $\text{C}_{\text{ArF-O}}$), 120.8, 117.1 (s, $\text{C}_{\text{Ar-H}}$), 102.6 ($\text{C}_{\text{ArF-C}_{\text{ArF}}}$), -0.6 (s, Si- CH_3)

Preparation of Poly(4,4'-bis(3-oxyphenyloxy)octafluorobiphenyl-co-tetramethyldisiloxane)

4,4'-bis(3-hydroxyphenyloxy)octafluorobiphenyl 0.9601 g (1.8666 mmol) was combined with 5 mL of toluene in a reaction flask. 1,3-bis(dimethylamino)-1,1,3,3-tetramethyldisiloxane 0.4241 g (1.9237 mmol) was combined with 5 mL of toluene in an addition funnel. The system was fitted with a condenser, a magnetic stirbar, and a tube to flush dry argon through the solvent. The reaction flask was heated to reflux in an oil bath, and the 1,3-bis(dimethylamino)-1,1,3,3-tetramethyldisiloxane solution added dropwise over a 15 minute period. The mixture was poured into isopropanol after an hour. The material was collected by filtration and dried overnight in the vacuum oven. The product was a clear rubbery compound with a brownish tint. Yield 0.460 g (40%) DSC $T_g = 20.0^\circ\text{C}$. TGA: $T_d = 420^\circ\text{C}$. GPC: $M_n = 18905$, $M_w = 53747$.

Anal. calc. for $\text{C}_{28}\text{H}_{20}\text{F}_8\text{O}_5\text{Si}_2$: C, 52.17%; H, 3.12%; F, 23.57%.

Found: C, 51.38%; H, 3.10%; F, 22.96%

^1H NMR: (CDCl_3) δ (, 8H, Ar-H), (s, 12H, Si- CH_3)

^{19}F NMR: (CDCl_3 w/ CFCl_3 int. std.) δ -138.9 (q, 4F, Ar-F), -154.0

(A_2B_2 , 4F, Ar-F)

^{13}C NMR: (CDCl_3) δ 157.7, 156.9 (s, $\text{C}_{\text{Ar-O}}$), 145.03, 141.63 (dd, $\text{C}_{\text{Ar-F}}$), 135.3

(s, $\text{C}_{\text{ArF-O}}$), 130, 115, 109, 108 (s, $\text{C}_{\text{Ar-H}}$), 102.6 ($\text{C}_{\text{ArF-C}_{\text{ArF}}}$), -0.7 (s, Si- CH_3)

Preparation of Poly(4,4'-bis(4-oxyphenyloxy)octafluorobiphenyl-co-decamethylpentasiloxane)

4,4'-bis(4-hydroxyphenyloxy)octafluorobiphenyl 0.5342 g (1.039 mmol) was combined with 5 mL of toluene in a reaction flask. 1,9-bis(dimethylamino)-decamethylpentasiloxane 0.4851 g (1.097 mmol) was combined with 5 mL of toluene in an addition funnel. The system was fitted with a condenser, a magnetic stirbar, and a tube to flush dry argon through the solvent. The reaction flask was heated to reflux in an oil bath, and the 1,9-bis(dimethylamino)decamethylpentasiloxane solution added dropwise over a 15 minute period. The mixture was poured into isopropanol after an hour. The white solid was collected by filtration and dried overnight in the vacuum oven. The product 0.904 g (98%) was a clear an viscous liquid. DSC $T_g = -48.8^\circ\text{C}$. TGA: $T_d = 320^\circ\text{C}$. $[\eta] = 0.173$. GPC: $M_n = 15989$.

Anal. calc. for $\text{C}_{34}\text{H}_{38}\text{F}_8\text{O}_8\text{Si}_5$: C, 47.11%; H, 4.38%; F, 17.55%.

Found: C, 49.84%; H, 5.13%; F, 15.03%

^1H NMR: (CDCl_3) δ 6.93, 6.87 (A_2B_2 , 8H, Ar-H), 0.11, 0.06, 0.05, 0.04 (s, 30H, Si- CH_3)

^{19}F NMR: (CDCl_3 w/ CFCl_3 int. std.) δ -138.9 (q, 4F, Ar-F), -154.0 (A_2B_2 , 4F, Ar-F)

^{13}C NMR: (CDCl_3) δ 151.5, 151.0 (s, $\text{C}_{\text{Ar-O}}$), 145.0, 141.7 (A_2B_2 , $\text{C}_{\text{Ar-F}}$), 135.3 (s, $\text{C}_{\text{ArF-O}}$), 120.8, 117.2 (s, $\text{C}_{\text{Ar-H}}$), 102.6 ($\text{C}_{\text{ArF-C}_{\text{ArF}}}$), 1.0, -0.5 (s, Si- CH_3)

Results and Discussion

The synthetic scheme leading to fluoroaryl ether/siloxane copolymers involves a four-step process as shown below:

Scheme 1.1

Step [1] involves the synthesis and purification of methoxy-terminated fluoroaryl ether oligomers. The methoxy group is used to generate the reactive phenolic functional group in the second step while preventing unwanted oligomerizations in the first. Use of 3 and 4-methoxyphenols allows for syntheses of monomers with differing regiochemistry at the terminus of the fluoroaryl ether. Step [2] is the removal of the methyl protecting group to yield the hydroxy-terminated fluoroaryl ether oligomers. Step [3] is the synthesis and purification of the amino-terminated siloxane/s from the corresponding chlorine-terminated reagent. Variation of the length of the siloxane chain provides variation in the mole fraction of siloxane in the final product. Reaction

of the products from steps [2] and [3] result in the desired copolymer.

Although the synthesis of the methoxy-terminated fluoroaryl ether oligomers had already been achieved by other methods,^{14,15} we decided to synthesize them through the use of solid/liquid phase transfer catalysis (SLPTC). The decision to use SLPTC was based on the results achieved by various bisphenols with decafluorobiphenyl in our group.¹⁶ Phase transfer catalysis is known for its speed and selectivity.¹⁷ As described in previous work,¹⁸ 18-crown-6 complexes with potassium ions, and acts as a carrier to transport ionic species into organic solvents. The complex also serves to separate the ion pair, making the counter ion more reactive. In this manner, 18-crown-6 complexes with potassium carbonate in the solid phase [1]. The acetone soluble complex then reacts with the phenol to form the potassium phenolate complex [2]. The potassium bicarbonate formed in the process returns to the solid phase.

Scheme 1.2

The unsolvated phenolate ion reacts rapidly with the decafluorobiphenyl. This is thought to occur by an $S_{RN}1$ -like mechanism.¹⁹ The electron rich aromatic ring of the phenolate ion complexes with one of the electron poor rings of the decafluorobiphenyl. An electron is then transferred from the phenolate ion to form the phenolate radical and the fluoroaryl radical anion.¹⁶

Scheme 1.3

Elimination of the fluoride ion followed by coupling of the two radicals results in the ether linkage. This mechanism is supported by the fact that the ether linkage is para (as determined by ^{19}F and ^{13}C NMR), although further substitution has been known to occur to some extent late in the reaction. A reaction mechanism via a Meisenheimer complex would predict meta substitution. The solutions have also been noted to develop a yellow color during the course of the reaction, which is suggestive of an electron transfer π -complex. Oxygen, a known radical trapping agent, has also been found to inhibit the reaction,¹⁹ supporting the presence of radical species. The potassium fluoride formed by the reaction is transported to the solid phase, where more potassium carbonate is picked up by the 18-crown-6, and the cycle repeated.

It has also been determined that a critical amount of water is necessary to achieve the maximum rate of the SLPTC reaction.²⁰ This effect is solvent dependent and has been noted in other SLPTC systems using quaternary ammonium salts²¹ as well as in those using 18-crown-6.²² Some workers theorize that the effect of trace water may be due to the formation of a quasi-phase between the solid and liquid layers which breaks up the crystal

lattice of the solid surface and allows more effective transfer of ions to and from the organic phase. In acetone, the optimal molar ratio of water to 18-crown-6 was found to be 2.3 to 1 for the reaction of phenols with decafluorobiphenyl.¹⁹

As shown in scheme 1.4 synthesis of 4,4'-bis(4-methoxyphenoxy)-octafluorobiphenyl [III] was achieved by combining 4-methoxyphenol [I] with decafluorobiphenyl [II] under optimal SLPTC conditions.

Scheme 1.4

It was possible to follow the course of the reaction using HPLC and thus determine the ideal time to stop the reaction. As shown by Fig. 1.1, decafluorobiphenyl [II] is consumed rapidly, and the reaction is complete in the course of an hour. This was important, as the reaction mixture will continue to react and cause further substitution. This reaction was also studied at 25°C for comparison to obtain a clearer picture of the reaction kinetics (Fig. 1.2). The HPLC response factors for the individual components were determined by making an equimolar mixture of pure components. In the same manner, synthesis of 4,4'-bis(3-methoxyphenoxy)octafluorobiphenyl [V] was achieved using 3-methoxyphenol [VI].

Scheme 1.5

This material was also obtained in good yield.

To prepare longer fluoroaryl ether oligomers, 4-(4-methoxyphenoxy)-nonafluorobiphenyl [VI] was synthesized as shown.

Scheme 1.6

By reacting the endcapped fluoromonomer with a difunctional phenol, an α,ω dimethoxy fluoroaryl ether can be formed. In this case, hydroquinone [VII] was combined with two equivalents of VI.

Scheme 1.7

Cleavage of the methyl protecting groups was accomplished by reacting the methoxy-terminated oligomer with boron tribromide. This procedure was first introduced by McOmie et. al.²³ and is a standard procedure for converting aromatic methyl ethers into phenols. This method is fairly mild compared to others because the reaction is usually done at or below room temperature. Some cleavage reactions which use reagents like aluminum tribromide can also react with halogens, forming unwanted byproducts, eg. substitution of iodide for bromide. However, this did not appear to be a problem for Kameneva et. al.^{14,15}. The reaction of aromatic methyl ethers is thought to occur via a complex between the ether oxygen and the boron tribromide²³ as shown in Scheme 1.8.

Scheme 1.8

S_N2 Nucleophilic attack of the methyl group causes cleavage of the weakened methyl oxygen bond by bromide ion, resulting in the formation of the aryl dibromoboron and methyl bromide. Simple hydrolysis of the boron ether then results in the formation of boric acid, hydrobromic acid, and the desired phenol. This worked well with III producing 4,4'-bis(4-hydroxyphenyloxy)-octafluorobiphenyl [IX].

Scheme 1.9

The same procedure was used to synthesize 4,4'-bis(3-hydroxyphenyloxy)-octafluorobiphenyl [X] from V.

Scheme 1.10

When considering the use of the chlorine terminated siloxane oligomers, which are readily available, and bis(dialkylamino)siloxanes it was determined

that the latter was better for making high molecular weight condensation polymers. Several factors make bis(dialkylamino)siloxanes better choices than the original dichlorosiloxanes in the formation of polymers. First, the dichlorosiloxanes are more polar, and thus more hydroscopic. They condense with water to form hydrochloric acid, and longer siloxane units. Without base to absorb the hydrochloric acid, cleavage of other silicon oxygen bonds can occur leading to shorter siloxane units.²⁴ Thus, a small amount of water can cause catalytic deterioration of the monomer. Bis(dialkylamino)siloxanes are less polar than their chlorine derivatives, and are correspondingly less hydroscopic. Dialkylamines are not known to break silicon oxygen bonds. Thus contamination by traces of water will result in the formation of longer siloxane units, but are not subject to further deterioration of the siloxane chains. Bis(dialkylamino)siloxanes are also more desirable from a kinetic standpoint, because the byproduct of the reaction of the aminosiloxane group with the phenol is dialkylamine, which can be distilled out of the reaction mixture. Thus the reaction is driven to completion by more efficient loss of the dialkylamine from the reaction system. Use of the dichlorosiloxane requires an added base such as pyridine, and the resulting pyridinium hydrochloride precipitates out of the reaction medium. Because the hydrochloric acid never really leaves the system, an equilibrium between silicon-oxygen bond formation and silicon-oxygen bond cleavage is reached. This is controlled by the solubility product of the base/hydrochloride and the base concentration in the reaction mixture. As a result, lower molecular weight material is formed.

In the course of synthesis of bis(dialkylamino)disiloxane, many different methods were attempted. Direct reaction of dimethylamine with bisdichloro-disiloxane resulted in the formation of voluminous precipitate of diethylamine hydrochloride.²⁵ The dimethylamine hydrochloride then had to be filtered off before the product could be isolated from the solvent mixture. This resulted in very poor yields due to loss of material as a result of exposure to atmospheric

water. Addition of magnesium to the reaction mixture failed to reduce the precipitate formation significantly.²⁶ By reacting the 1,3-bisdichlorotetramethyldisiloxane [XI] with lithium diethylamide [XII]²⁷, however, fewer losses were incurred as the filtration process was eliminated because the lithium chloride byproduct did not need to be removed before distillation.

Scheme 1.11

Model studies later showed that dimethylamine, although more difficult to prepare, resulted in polymers of significantly higher molecular weight than those made with diethylamine. This is most likely effected by a combination of steric factors and in the lower volatility of the diethylamine (bp: 56°C) versus dimethylamine (bp: 7°C). Therefore, 1,3-bis(dimethylamino)tetramethyldisiloxane was prepared from [XI] by reacting it with lithium dimethylamine [XIV].

Scheme 1.12

Model studies were conducted with XIII and 4-isopropylphenol [XVI] to optimize conditions for polymerization.

Scheme 1.13

HPLC analysis of the product mixture yielded trace 4-isopropylphenol, the major component, and a small amount of a third component which eluted at a

much later time. The ^1H NMR yielded the expected spectrum, but showed a second peak in the siloxane region which could not be accounted for. Mass spectrum analysis of the product mixture gave the results as shown in Figs. 1.3 and 1.4. The first component peak represents 97% of the total reaction mixture, and has mass spectrum with a molecular ion of 402, which agrees with the mass spectrum expected for the desired product. The second component has a molecular ion of 550, which agrees with that of a tetrameric material formed by a reaction with trace water to form a siloxane linkage.

Scheme 1.14

Once reaction conditions had been optimized and 1,3-bis(4-isopropylphenoxy)disiloxane [XVII] had been synthesized in good yield, analogous polymerizations were accomplished using bisphenol-A [XX]. It was found that polymers of only low molecular weight could be synthesized from [XIII] as determined by viscosity measurements.

Scheme 1.15

Substituting 1,3-bis(dimethylamino)tetramethyldisiloxane [XIII] for 1,3-bis(diethylamino)tetramethyldisiloxane [XV] resulted in an increase of the inherent viscosity from 0.19 to 0.56 poise.

Scheme 1.16

The success of this reaction depends on the use of preconditioned glassware. Bis(dialkylamino)siloxanes are so reactive that they react with silanol groups on the glass surface. On a bulk scale this would not be a problem, but when millimolar concentrations of reagents are used, as in this trial study, monomer consumed by this side reaction is great enough to upset the siloxane monomer concentration and thus reduce the molecular weight (see eq. 1.3). By pretreating the glassware the glassware with aminosiloxane, the organosiloxanes bound to the surface prevent loss of monomer. This need be done only once with each piece of glassware as the chemical bonding is quite strong, and it would take excessive heat (>400°C), strong base (methanolic KOH), or fluoride ion (HF or KF) to remove the protecting layer.

Polymerization was achieved by combining 1 equivalent of the bisphenol with 1.05 equivalents of the bis(dimethylamino)siloxane. It was found to be a common practice in siloxane chemistry to add a slight stoichiometric excess of the siloxane reagent.²⁸ This excess is presumably used to offset the amount of dialkylamino groups consumed by reaction with water. The polymerization is shown below.

Scheme 1.17

In this manner, XV was combined with XI to produce poly(4,4'-bis(4-oxy-

phenyloxy)octafluorobiphenyl-co-tetramethyldisiloxane [Poly(B4HPB-co-DS)] creating a tough clear plastic. The meta derivative of the same polymer poly(4,4'-bis(3-oxyphenyloxy)octafluorobiphenyl-co-tetramethyldisiloxane [Poly(B3HPB-co-DS)], was synthesized by combining X and XV yielding a clear rubbery material. Finally, by combining IX with 1,9-bis(dimethylamino)decamethylpentasiloxane [XXII], poly(4,4'-bis(4-oxyphenyloxy)octafluorobiphenyl-co-decamethylpentasiloxane [Poly(B4HPB-co-PS)], a clear viscous liquid, was synthesized. Thus by manipulating various structural features in the polymer backbone, the physical properties of the copolymer can be altered. By increasing the length of the siloxane segment, the weight percent of siloxane in the polymer is increased and the flexibility of the polymer is increased. By manipulating the orientation of the hydroxyl groups we can effect the morphology of the fluoroaryl ether segments. Para phenols should have a greater tendency towards crystallization than the corresponding meta phenol. Thermal analysis of these materials show that the physical properties of these materials are directly related to the siloxane content (Table 1.2). As expected the polymer synthesized with V had a lower T_g than the corresponding polymer made with III. This is due to the fact that the copolymers of meta-linked siloxanes provide a greater number of rotational conformations than those of the para. This introduces more randomness into the polymer matrix resulting in a lower T_g . It is interesting to note that V showed a T_c of 60.5°C. Although it is quite common for polymers to display crystallization temperatures below their melting points, it is unusual for small molecules to exhibit such behavior. The decomposition temperature of the copolymers was, in the cases of the copolymers incorporating the disiloxane in the backbone, above that of the polydimethylsiloxane. This is due to the fact that the thermal decomposition of polydimethylsiloxane proceeds via an intramolecular backbiting mechanism²⁹ whereby cyclic products and short chain oligomers are formed.

Scheme 1.18

In those polymers, that contain only two siloxane units per repeat unit, backbiting is unfavorable, as strained four-membered rings would have to be formed. Thus the thermal stability of the polymers containing short siloxane segments is enhanced.

Although the ^1H and ^{19}F spectra provided some details as to the structure of the copolymers, the most complete structural analysis was obtained by high resolution ^{13}C NMR as shown in Figs 1.5 to 1.7. Poly(B4HPB-co-DS) and poly(B4HPB-co-PS) have nearly identical spectra. At 158 to 155 ppm we find the ethereal carbons of the nonfluorinated aromatic ring. The effect of fluorine on the chemical shifts of carbon can be quite unusual. Most NMR's are incapable of decoupling fluorine and hydrogen in the same carbon spectra. This can be used to distinguish the fluorinated carbons from those that are hydrogenated by comparing coupled and decoupled spectra. The two doublets that appear at 145 and 141.5 ppm are the aromatic carbons in the fluorinated rings and have a coupling of 225 Hz due to J_{1-2} coupling with the attached fluorine. The J_{1-3} carbon-fluorine coupling was useful in determining which peaks correspond to the quaternary carbons adjacent to fluorinated carbons. The ethereal carbons on the fluorinated aromatic rings and the bridging carbons on the fluorinated aromatic ring appear as triplets at 130 and 102.6 ppm respectively because of coupling to adjacent fluorines. The aromatic carbons bearing hydrogen appear at 120 and 117 ppm. Finally, the methyl groups on the siloxane units adjacent to the aromatic ring appear at -0.7 ppm. Those polymers with longer siloxane units are have silyl methyl carbons

that are not adjacent to aromatic rings that appear at 0.7 ppm. For poly(B3HPFB-co-DS) the spectrum is very similar to that found above, except that the aromatic ethereal carbons of the nonfluorinated ring appear at 158 and 155.5 and the aromatic carbons bearing hydrogens appear at 130, 115, 109, and 108 ppm. The extraneous peaks found in the spectrum are due to hydrolysis as the sample was exposed to atmospheric moisture for some time before the spectrum was run.

The ^1H NMR spectra, although not as useful because they do not show as complete of a structural picture as does the ^{13}C spectra, do give quantitative information that the ^{13}C spectra lack. As noted in the model polymerization study, there is some formation of Si-O-Si bridges along the backbone due to water present as a contaminant in the reaction mixture. In those polymers containing only short siloxane segments this contamination can be seen in the ^1H NMR spectra (Figs. 1.8 to 1.10), and the ratio of that peak found at 0.24 and 0.0 ppm correspond to the 1:0.05 ratio expected based on the excess siloxane reagent added. Complete exclusion of water should result in a more pure copolymer. For poly(B4PFB-co-DS) we see an A_2B_2 splitting pattern at 7.0 to 6.8 which is characteristic of a para-substituted aromatic ring. The siloxane hydrogens appear at 0.24 ppm. The ratio of the areas of the two sets of peaks is 2:3, which is the expected ratio. Poly(B4PFB-co-PS) has a nearly identical spectra except that the silyl methyl peaks appear at 0.11 and 0.0 ppm. Poly(B3PFB-co-DS) is slightly different with the aromatic carbons appearing as a triplet, two doublets and a singlet in the region of 7.2 to 6.5 ppm.

The ^{19}F spectra are essentially equivalent for all three copolymers. These show two peaks of equivalent area at -138.8 and -153.9 ppm. The former peak is split into a quintet due to J_{1-5} coupling, and by the fluorines on the adjacent fluoroaromatic ring. The later peak is split into a doublet of doublets and corresponds to fluorine adjacent to the ethereal carbon on the fluoroaromatic ring. The absence of any other peaks in the ^{19}F NMR show

that all ether linkages to the fluoroaryl rings are exclusively para in nature (Figs. 1.11 to 1.13).

The ultra-violet/visible spectra shown in Figs 1.14 show that these copolymers have a high absorption in the range of 230 to 320nm. This is a distinct advantage for contact lens applications as it has been well established that ultra-violet light can damage the ocular lens in the eye resulting in cataracts. Contact lenses made of these materials would protect the eyes from light in this region of the UV spectrum.

Conclusions

The procedure described above is a viable method of preparing fluoroaryloxy/siloxane copolymers. Manipulation of monomers allows for the synthesis of a variety of copolymers of this type. Although this work has described the synthesis of longer fluoroaryl ether oligomers, these were not purified to an extent which made them suitable for polymerization. Copolymers with more block character would probably exhibit the thermoplastic elastomeric properties that were attempted in this synthesis. Increasing the length of the fluoroaryl ether segments should also increase the amount of phase separation. The extra peaks in the aromatic region of the poly(B3HPB-co-DS) appeared after the material had stood for a few months. Some samples of poly(B4HPB-co-PS) had also exhibited deterioration, but not all of them. This is most likely due to hydrolysis of the polymer by atmospheric moisture, as there is some evidence for this in the literature as to this side reaction,²⁴ and the position of the extraneous peaks correspond with those found in the phenolic monomer. This problem may be overcome by reducing the number of siloxane-aryl ether linkages along the backbone, as both siloxanes and fluoroarylethers are hydrolytically stable. The poly(B4HPB-co-DS), however, did not seem to be affected to any extent. This may be due in part to the higher T_g of this polymer reducing the molecular mobility of the polymer chains. Hydrolysis could be eliminated by linking the fluoroaryl ether segments and siloxane segments directly. This might be achieved by using a bromine terminated fluoroarylether with a chlorine terminated siloxane via a grignard synthesis.^{30,31} Those copolymers with high fluoroaryl ether content that were synthesized in this experiment could be used in those applications requiring a rigid structure. The incorporation of short siloxane segments serves as a plasticizing agent that will not leach out of the material.

Table 1.1 Differential Scanning Calorimetry and Thermal Gravimetric Analysis of Monomers and Copolymers

Compound	T _g ^a	T _c ^a	T _m ^a	ΔH _m ^b	T _d ^c
III	--	n/o	91.3	63.4	--
V	--	n/o	88.4	69.6	--
IX	--	n/o	209.8	102.2	--
X	--	60.5	106.9	42.8	--
Poly(B4HPB-co-DS)	37.9	n/o	n/o	--	490
Poly(B3HPB-co-DS)	20.0	n/o	n/o	--	420
Poly(B4HPB-co-PS)	-48.8	n/o	n/o	--	320

^a in °C. Measured by measuring 5mg sample utilizing a 10°C/min temperature ramp.

^b in J/g. Measured by measuring 5mg sample utilizing a 10°C/min temperature ramp.

^c in °C. Measured as 10% weight loss.

Table 1.2 GPC and Viscosity Analysis

Compound	M _n	M _w	M _w /M _n	[η]
Poly(B4HPB-co-DS)	56087	111030	1.98	0.445
	15920	30830	1.94	--
Poly(B3HPB-co-DS)	18905	53747	2.84	--
	5629	13141	2.33	--
Poly(B4HPB-co-PS)	15989	--	--	0.173

Fig. 1.1 Kinetic Plot of the Reaction of
Decafluorobiphenyl with 4-Methoxyphenol in
Acetone at 56°C

Fig. 1.2 Kinetic Plot of the Reaction of
Decafluorobiphenyl with 4-Methoxyphenol in
Acetone at 25°C

Fig. 1.3 Mass Spectrum of the Product formed by the Reaction of 4-isopropylphenol with 1,3-bis(diethylamino)tetramethyldisiloxane

Fig. 1.4 Mass Spectrum of the Byproduct formed in the Reaction of 4-isopropylphenol with 1,3-bis(diethylamino)tetramethyldisiloxane

Fig. 1.5 75MHz ^{13}C Spectra of Poly(B4HPB-co-DS)

Fig. 1.6 75MHz ^{13}C Spectra of Poly(B3HPB-co-DS)

Fig. 1.7 75MHz ^{13}C Spectra of Poly(B4HPB-co-PS)

Fig. 1.8 300MHz ^1H Spectra of Poly(B4HPB-co-DS)

Fig. 1.9 300MHz ^1H Spectra of Poly(B3HPB-co-DS)

Fig. 1.10 300MHz ^1H Spectra of Poly(B4HPB-co-PS)

Fig. 1.11 282MHz ^{19}F Spectra of Poly(B4HPB-co-DS)

Fig. 1.12 282MHz ^{19}F Spectra of Poly(B3HPB-co-DS)

Fig. 1.13 282MHz ^{19}F Spectra of Poly(B4HPB-co-PS)

1.14 Ultra-Violet/Visible Spectrum of Poly(B4HPB-co-PS)

Part 2: The Radiation Chemistry of Methacrylic Acid/Acrylonitrile Copolymers

Introduction

The effects of long term exposure of many types of polymers to ionizing radiation is still not yet known. However, extensive studies on several of the most common types of polymers has given us enough of an understanding to make generalized statements about the radiation chemistry based on the types of structural features present in polymers. Less is known about the radiation effects on copolymers where interactions of adjacent monomers can severely alter the chemistry of the radical species. A few studies on copolymers^{32,33} show that the radiation sensitivity of a particular copolymer may be very different from the expected sensitivity based on the parent homopolymers. In this study, the effects of gamma-radiation on the random copolymers of methacrylic acid and acrylonitrile were examined. The bulk of this work was conducted at the University of Queensland in St. Lucia, Australia under the guidance of Dr. D. J. T. Hill, Dr. P. Pomery, and Prof. J. H. O'Donnell.

Background

When high energy radiation is absorbed by an organic molecule such as a polymer, it is promoted into an excited state, the excited polymer can shed this excess energy in many different ways (Scheme 1). It can re-emit the energy as a photon or photons, it can lose an electron and become a radical cation, or the energy can result in the breaking of bonds and the formation of radical fragments. The electrons generated by the latter pathway can later be captured by other molecules which form radical anions.³⁴

Scheme 2.1

The reactive radical species undergo abstraction, disproportionation, and coupling reactions until all but the most stable radicals are left. The rate at which these radical species decay is dependent upon the relative stabilities of these radicals. Some are highly reactive and disappear quickly, while others are more stable and react very slowly.

Experiments involving radiation chemistry use the expression "G[value]" to report the formation of various products or events per 100eV of energy absorbed by one gram of polymer. Many types of G[values] can be determined for a particular system. Those most commonly applied to polymers are shown in table 2.1.

Table 2.1 Techniques Used to Determine G[values] for Polymers

<u>G[variable]</u>	<u>technique used</u>	<u>effect measured</u>
G[X]	size exclusion chromatography	cross-linking of polymer
G[S]	size exclusion chromatography	chain scission of polymer
G[gas]	gas chromatography	yield of volatile products (<i>can be used to express single products or total gas yield</i>)
G[radical]	electron spin resonance	yield of radicals

Each technique provides information as to the nature of the radiation induced reactions.

Electron spin resonance [ESR] is one of the most valuable methods for analyzing the effects of radiation because it provides both qualitative and quantitative information about the interaction of a substance with ionizing radiation. ESR detects unpaired electrons, both those found in radical species, and those in partially filled orbitals such as those found in many transition metal species. As in NMR, coupling of adjacent nuclei with nuclear spins greater than zero results in multiplets which can be used to elucidate the structural features adjacent to the radical species. The unpaired electron, however, is not effected electron density (as is the proton in NMR), and so most radical species lay on top of one another. Furthermore, by comparing the area of the ESR spectrum of the polymer with that of a standard of known concentration, the total radical concentration in the sample can be determined. Often, experiments are conducted at several temperatures: ambient temperature to find the radicals present under conditions where the material is actually used, and at lower temperatures to help trap short lived radicals which are involved in the overall chemistry, but decay before they can be observed. With the aid of computers it is also possible to "subtract" ESR spectra, and thus

give a clearer picture of the differences between two spectra.

The types of reactions that the irradiated polymer undergoes is of course dependent upon the original structure of the material. The effects of these radical reactions can vary quite a bit from polymer to polymer. Polymers with quaternary carbons along the backbone have a tendency to undergo main chain scission, and thus the molecular weight of these polymers are reduced. Polymers with secondary and tertiary carbons are much more resistant to main chain scission.³⁵ Therefore, coupling reactions play a greater role, causing the molecular weight of these polymers to be increased due to crosslinking. Functional groups can also play a role in changing the radiation chemistry of a polymer. Aromatic rings are known to be resistant to the effects of radiation because they can shed excess energy through radiative processes without damage to the polymer. Ester functionalities, however, go through chemical transformations which prevent the first formed radicals from ever recombining by elimination of carbon monoxide and carbon dioxide. Consequently, the effects of radiation are more severe.

The glass transition temperature [T_g] and the amount of crystallinity in the polymer sample can also effect the its radiation chemistry. Radicals trapped in the amorphous regions of a polymer matrix, when heated above the T_g of the material, are often lost due to coupling and disproportionation reactions caused by increased mobility within these regions. Polymer chain segments in crystalline regions however, are locked into a rigid matrix, and recombination of radical pairs is more common. Migration of radical species can also occur in crystalline regions of the polymer through successive abstraction of neighboring hydrogen atoms.^{36,37} The radicals finally reach reactive centers and are destroyed by mechanisms mentioned previously, or reach stable centers where they remain trapped.

There has been little work in the area of radiation chemistry of copolymers. Examination of the microstructure of the copolymer is extremely important in determining the physical properties of the copolymer, and is just as important in influencing the radiation chemistry. There are several types of copolymers: random, alternating, and block. Random copolymers have the two repeat units along the backbone distributed in an unordered pattern along the backbone.

-A-A-M-A-M-A-M-M-A-M-A-A-A-M-A-M-A-M-M-A-M-M-M-A-M-A-A-M-

Because the monomer units are evenly distributed along the polymer chain a series of copolymers with various amounts of the two monomers in the backbone, the concentration of radical species indicative of each type of repeat unit should change in a steady and uniform manner with respect to copolymer composition. Radiation enhancement or protection effects should also be expected to undergo change as a function of copolymer composition. Alternating copolymers show greater structural regularity with two repeat units distributed in an alternating pattern along the backbone.

-M-A-M-A-M-A-M-A-M-A-M-A-M-A-M-A-M-A-M-A-M-A-M-A-

Because each monomer unit of one type is surrounded by monomer units of the other type, alternating copolymers should show the maximum amount of intramolecular interaction of the copolymer types. Block copolymers are arranged in such a way as to give long segments of one monomer type attached to long segments of another monomer type.

Because there are very few monomer units of one type interacting with monomer units of the other type, block copolymers should show very little intramolecular interaction between the two different monomer units. In fact if there was any interaction at all, it would in an intermolecular manner. These polymers would behave very similarly to a blend of two homopolymers. Although few copolymer systems give ideal microstructures as the those described above, the chemistry of the copolymers will most certainly be affected by the which arrangement the particular copolymer resembles.

Experimental

Most of the copolymers used in this study were synthesized and characterized by Dr. Anthony Lang at the University of Queensland. Polymethacrylic acid (PMAA) was prepared by Dr. Cathy Windsor at the University of Queensland by emulsion polymerization utilizing sodium persulfate.³⁸ Polyacrylonitrile (PAN) was prepared by Dr. Paul O'Sullivan at the University of Queensland by polymerizing acrylonitrile in water using a potassium persulfate/potassium bisulfite.³⁹ The two copolymers that were not prepared by Dr. Lang were synthesized using the same general procedure. Methacrylic acid (MAA) from Fluka was vacuum distilled at 72°C at 24 mmHg. Acrylonitrile (AN) from Merck was distilled under a nitrogen blanket at 77°C and 760 mmHg. Benzoyl peroxide (BPO) was used as received from Ajax Chemicals. The polymers containing 63%MAA/37%AN and 89%MAA/11%AN were prepared by combining the above reagents in sealable long neck 100 ml round bottom flasks, in the proportions shown in Table 2.1. The samples were degassed using the freeze/thaw method three times, and then sealed under a vacuum of 10^{-4} mmHg. Both samples were then warmed in a 60°C water bath and shaken for the time indicated above. White solids had formed in both reaction vessels during the course of polymerization. Both samples were cooled to at least -20°C until they were worked up. The sealed flasks were opened, the solid material dissolved by adding 30ml of methanol, and then precipitated into 500ml of chloroform. The samples were then dried under vacuum overnight at 75°C. These two samples were then reprecipitated a second time and dried under vacuum overnight at 60°C before use, as were those obtained from the University of Queensland. It was determined that methanol was the best solvent for those polymers that contained more than

60% methacrylic acid. Dimethyl sulfoxide was determined to be the best solvent for those polymers that contained less than 60% methacrylic acid. The best nonsolvent was chloroform, and it could be used across the entire composition range of copolymers. Once the copolymers were purified, they were ground up into a fine powder using a mortar and pestle. Liquid nitrogen was used to freeze the samples and make them more brittle during grinding. The powdered samples were then sifted through a fine mesh. These were then dried again in the vacuum oven at 60°C. The samples were packed into ESR tubes which had tips of high quality spectroil quartz (30 mm) and a constant inner bore of 3 mm. The tubes were carefully weighed before and after packing to determine the amount of material in the tube. The material was added a little at a time and then compressed, using a metal rod, to ensure a high packing density, and a pipe cleaner was used to get rid of any residual material on the inside walls of the tube. The samples were packed to a height of about 28 mm. These tubes were then fitted with joints and attached to a vacuum line. The samples were then heated to 65°C under high vacuum for at least 24 hours before being sealed under a vacuum of at least 10^{-5} mmHg.

Before the samples were irradiated with ^{60}Co γ -rays from a Gammacell 220 gamma source (Atomic Energy of Canada Limited), Fricke dosimetry was used to determine the dose rate (see Appendix A). The dose rate was calculated for the day of each experiment using the equation:⁴⁰

$$D_s = D_0 e^{(-3.6078 \times 10^4)(t)} \quad [2.1]$$

D_0 = dose rate as measured using Fricke dosimetry

t = number of days since the dosimetry was conducted

The background glass signal for the sample tubes was measured using a Brüker ER 200 D x-band ESR. The samples were then irradiated in steps of approximately 2 kGy. While being transferred to and from the gamma-cell to the ESR, the tubes which were irradiated at room temperature were kept in liquid nitrogen in the dark. Those samples which had been irradiated at 77 K were kept in liquid nitrogen at all times. The ESR spectrum of the irradiated samples was then taken, and measured against Strong Pitch (Varian $3 \pm 0.75 \times 10^{15}$ spins/cm). Those samples that were irradiated at room temperature were measured at room temperature, and those that were irradiated at 77 K were measured at 77 K. All samples and the standard were measured with a modulation of 0.2 mT at a power level of $19.9 \mu\text{W}$ and a sweep width of 25 mT. SIMOPR, a PC computer based data acquisition and manipulation program,⁴¹ was used to store and integrate the spectra obtained from the ESR. The samples were then put back into the gamma source, and the procedure repeated until a cumulative dose of 10 kGy had been obtained. Double integration of the spectra provided the area. The number of spins/cm was calculated using the equation:⁴²

$$N_{\text{sam}} = \frac{N_{\text{std}}(A_{\text{sam}})(G_{\text{std}})}{A_{\text{std}}(G_{\text{sam}})} \quad [2.2]$$

N = number of spins/cm

A = area of the integrated spectrum

G = gain used when recording the spectrum

The number of spins/g was then calculated by dividing number of spins/cm by the density of the sample (in g/cm). The corrected dose rate was recalculated

for each sample to account for the difference in the mass balance of the sample with respect to the mass balance of the Fricke reagent (essentially water) by using the equation:⁴³

$$D_{\text{corr}} = \frac{D_s \sum X_j (\sum n_i M_i \mu_i / MW_i)}{(0.0296)} \quad [2.3]$$

D_s = calculated dose

n_i = number of atoms for a specific element in the repeat unit

M_i = the mass of a specific element

μ_i = mass correction factor for a specific element using 1.25 MeV photons⁴⁴

X_j = mole fraction of the repeat unit

MW_i = molecular weight for the repeat unit

Once the actual dose rate had been calculated, a plot of radical concentration (spins/g) versus dose (kGy) was made, and a best fit line was applied using a linear least square analysis program. The slope of this line was used to calculate G[radical] from the equation:⁴³

$$G[\text{radical}] = d[\text{radical}]/dD \times 16 \times 10^{-18} \text{ kGy}/100\text{eV} \quad [2.4]$$

After a sufficient number of radicals were present, a power plot was made for each sample. This was done by plotting the area of the spectrum verses the square root of the microwave power. In this manner it was possible to determine the maximum power level which could be used to get the highest possible resolution without saturating the radicals (eg. highest power level

which remained on a straight line with the first few points of the series). It was determined that $19.9 \mu\text{W}$ was satisfactory across the entire range of copolymer compositions at both room temperature and 77 K.

Selected samples that were irradiated at 77 K were also used in variable temperature experiments and photobleaching experiments. Using the variable temperature unit, the samples were heated to the desired temperature and held there for at least 5 minutes. The sample was then cooled back down to 110 K and the spectrum recorded. In this manner the effects of temperature on the Boltzman distribution were avoided. This procedure was used to obtain spectra from 110 K to 330 K in increments of 20 K. Strong pitch was also recorded at 110 K. Subtraction spectra were generated by computer manipulation using SIMOPR. Photobleaching experiments were conducted by irradiating first with 600 nm light for short periods, and then slowly increasing photolysis times. After no further changes were recorded the sample was irradiated with 495 nm and 360 nm light in the same fashion.

Due to the unusual behavior exhibited by the copolymers at several compositions, it was necessary to check the glass transition temperatures of the copolymers. This was achieved by differential scanning calorimetry using a Perkin Elmer DSC7/DX. About 5 mg of the powdered polymer was encapsulated in an aluminum sample pan. The sample was annealed at 100°C for 20 minutes to remove any absorbed water and/or solvent. The sample was then scanned over an appropriate temperature range at a rate of 10°C/min. The temperature calibration was checked before running samples by checking the onset of melting of an indium standard (onset 156.6°C). Since it is known that anhydride formation is possible below 200°C all samples were ramped only once above this temperature.⁴⁵ It was not possible to determine the T_g of samples with greater than 89% methacrylic acid, as the T_g was

swamped by the heat generated by thermochemical reactions.

The copolymer composition for the two copolymer samples not received from Dr. Lang were achieved using similar procedures. Samples were dissolved in DMSO-D₆ to make a 20% (by weight) solution. Using a Brüker 300 MSL NMR operating with a variable temperature unit set to 60°C, employing a pulse program to provide inverse gated decoupling and a delay time of 10.25 seconds⁴⁶ to eliminate nuclear overhauser effects, ¹³C spectra were generated [Fig. 2.1]. Integration of the peaks responsible for the carbonyl (179.5 to 175.1 ppm) and nitrile (123.2 to 120.5 ppm) carbons yielded the percent composition of methacrylic acid and acrylonitrile units in the copolymer. Further dissection of these peaks provides information about the molecular arrangement along the backbone. Nearest neighbor effects cause changes in the chemical shifts of the carbonyl and nitrile peaks. These are called triads, because they are composed of a central constituent flanked by two adjacent units which alter the chemical shift of the central constituent. Determining the relative areas of the carbonyl peaks yielded the methacrylic acid (M) centered triads MMM, AMM (and its equivalent MMA), and AMA. The same was done with the nitrile peaks to determine the acrylonitrile (A) centered triads. These distributions are shown Table 2.2. The triad distributions agree well with those obtained by Dr. Lang.⁴⁷ By employing the equations shown below,⁴⁸ the reactivity ratios for the monomer units were determined. The fraction of M-centered triads is related to the probability of a acrylonitrile unit adding to an methacrylic acid propagating radical [P(M/A)] by the equations:

$$F_{AAA} = [1 - P(M/A)]^2 \quad [2.5]$$

$$F_{MAA} = F_{AAM} = P(M/A) [1 - P(M/A)] \quad [2.6]$$

$$F_{MAM} = [P(M/A)]^2 \quad [2.7]$$

Since the triad fractions can be experimentally determined by NMR, we can solve for $P(M/A)$ by taking an average from the results of the equations below:

$$P(M/A) = 1 - [F_{AAA}]^{0.5} \quad [2.8]$$

$$P(M/A) = \frac{1 + [1 - 2(F_{AAM} - F_{MAA})]^{0.5}}{2} \quad [2.9]$$

$$P(M/A) = [F_{MAM}]^{0.5} \quad [2.10]$$

The probability of an acrylonitrile unit adding to a methacrylic acid radical is related to the monomer reactivity ratio $[r_A]$ by the equation:

$$P(M/A) = \frac{1}{1 + r_A x} \quad [2.11]$$

Where x is the monomer feed ratio $[A]/[M]$. Again, this equation can be rearranged to solve for the reactivity ratio as shown below:

$$r_A = \frac{1 - P(M/A)}{P(M/A)x} \quad [2.12]$$

A similar series of equations was employed to determine the reactivity ratio for the methacrylic acid unit. From the distributions shown above, the monomer

reactivity ratios r_A and r_M were found to be 0.14 and 1.6 respectively. Using these reactivity ratios, the deviation from that of a completely random copolymer $[\chi]$ was determined from the following equation:

$$\chi = \frac{r_A X + 2 + r_M/X}{r_A X + 1 + r_A r_M + r_M/X} \quad [2.13]$$

An χ value of 1.34 was determined for the copolymer composition from the 63% MAA copolymer. Since χ is greater than one, the copolymer has a slightly alternating structure. If χ had been equal to one, it would have been a random copolymer, if χ had been equal to two, it would have been a completely alternating copolymer, and if χ had been equal to zero, it would have been a block copolymer.

Results and Discussion

A series of eight methacrylic acid/acrylonitrile copolymers, polyacrylonitrile, and polymethacrylic acid were irradiated at 77 K and 303 K (ambient temperature in the source), and their ESR spectra recorded at approximately 2 kGy intervals to a maximum of 10 kGy. As described earlier, these spectra were used to create plots of radical concentration (in spins/g) versus dose (in kGy). From the slope of these graphs, the dose dependence of the net radical concentration was determined as shown in Figs. 2.2-2.11. The G[radical] for those copolymers irradiated at 77 K is greater for all compositions than that of the homopolymers as shown in Fig. 2.12. Furthermore, there seems to be a maximum G[radical] at the composition containing 75% methacrylic acid; general examination of the 77 K ESR spectra [Fig.13a] shows an increase of a triplet pattern associated with Radical 1 with respect to PAN:

This feature is clearly shown by the subtraction of the spectrum of polyacrylonitrile from that of the 11% methacrylic acid copolymer [Fig. 2.14a] (those with peaks going from positive to negative are being lost, and those with peaks going from negative to positive are being formed). There are also other peaks which are associated with the acrylonitrile propagating radical (radical 2) as well [Fig. 2.13b].

Comparing the 36% and 44% MAA spectra [Fig. 2.14b] the carbonyl radical ($R\text{-COO}\cdot$) associated with methacrylic acid shows up quite clearly. There is a loss of a sharp triplet species as well, which may be due to the acrylonitrile backbone radical 1. The difference spectra of 75% and 63% MAA [Fig. 2.14c] indicate that there is a loss of a very ill defined radical(s), however, this same species was lost by photobleaching 63% MAA with 600 nm light after irradiating at 77 K [Fig. 2.24a] and may be the carbonyl radical anion (radical 3).

There is very little difference in the high methacrylic acid copolymer spectra from that of pure polymethacrylic acid, although the 89% MAA spectra does show the presence of some methacrylic acid propagating radical [Fig. 2.14d].

The room temperature spectra show even more significant differences. All the copolymer samples irradiated at room temperature have lower $G[\text{radical}]$ values than the homopolymers as shown in Fig. 2.12. The minimum for this series is located at approximately 63% MAA. The decrease in radical concentration cannot be due to the effects of the copolymer T_g s, as all the polymers studied had T_g s at least 80°C above room temperature [Fig. 2.16]. This was confirmed by warm-up experiments where a steady decrease in radical concentration was evident. The 11%, 24%, 36%, and 44% methacrylic acid ESR spectra [Figs. 2.2b, 2.3b, and 2.4b] all resemble the ESR spectra of polyacrylonitrile, with slight differences in the fine structure. None of these additions to the fine structure resemble those radicals found in the methacrylic acid ESR spectrum. As shown in the subtraction spectra of PAN and 24% MAA

[Fig. 2.15a], the major component being lost is a species composed of a doublet of quintets. This species has been assigned by Lang et. al.⁴⁹ to the backbone radical (radical 4) formed by loss of the nitrile group as shown below [Fig. 2.13c]:

Comparing the 36% and 44% MAA spectra [Fig. 2.15b], some evidence for the appearance of the lines associated with sharp features of methacrylic acid 4 by 5 line propagating radical (radical 5) [Fig. 2.13d] begin to appear.

The 63% and 75% methacrylic acid ESR spectra [Figs. 2.7b and 2.8b] contain the acrylonitrile propagating radical and more of the methacrylic acid propagating radical. Finally, the 85% and 91% methacrylic acid room temperature ESR spectra [Figs. 2.9b and 2.10b] are exactly like that of polymethacrylic acid itself [Fig. 2.11b], and appear to be composed completely of methacrylic acid propagating radical.

Selected copolymer samples, 24%, 44%, and 75% methacrylic acid, were irradiated at 77 K and then warmed up to room temperature. There is a steady decrease in radical concentration upon warming in all three samples as shown by Fig. 2.17. Care must be taken in interpreting this data directly, because further analysis of the subtraction spectra indicate that radical destruction is

occurring simultaneously with radical transformation reactions. Analysis of the subtraction spectra in the warm-up experiments proved to be of the greatest use in determining some of the mechanisms by which the radicals were decaying. As shown in Figs. 2.18, 2.19, and 2.20, we can see a number of radicals being lost and generated. Individual analysis yields losses of various radicals in differing proportions.

For the 24% methacrylic acid copolymer, the subtraction spectra from 150 K and 130 K [Fig. 2.21a] indicate the formation of the acrylonitrile propagating radical, and the loss of some sort of singlet species. It is interesting to note that other workers have reported that irradiated polyacrylonitrile yields very little propagating radical.⁴⁹ Further warming shows a reduction of radical 2, and the loss of a triplet for 210 K to 230 K [Fig. 2.21b] which has been assigned to radical 1. Warming to 290 K from 270 K [Fig. 2.21c] shows a loss of acrylonitrile propagating radical, and either a singlet or triplet species. Finally, examination of the subtraction spectra from 310 K and 330 K [Fig. 2.21d] we see the characteristic doublet of quintets that has been assigned to radical 4. In general the spectra look very similar to those spectra obtained from pure polyacrylonitrile with a few differences in concentration. The apparent lack of any methacrylic acid radicals and the formation of excessive amounts of acrylonitrile propagating radicals can be explained. It is known that the major radiation product radical of polymethacrylic acid is the methacrylic acid propagating radical. This is formed by the decay of the acid radical via decarboxylation and beta scission reactions as outlined below:⁵⁰

Scheme 2.2

Assuming that methacrylic acid units behave the same way in the copolymers as they do in the homopolymer, the methacrylic acid units would form the carboxylic acid radical, and decarboxylate upon warming. Due to the low concentration of methacrylic acid units along the backbone of the copolymer, if beta-scission did take place, the major product of this reaction would have to be the radical 2 as shown below:

Scheme 2.3

This accounts for the excessive amounts of acrylonitrile propagating radical, and the lack of methacrylic acid radicals in the ESR spectra seen at room

temperature in those samples with a high acrylonitrile content. This is also supported by the triad distributions which indicate that the copolymers are alternating in nature. Thus methacrylic acid units have a high probability of acrylonitrile located in adjacent positions.

Examination of the warm-up experiment of the 44% methacrylic acid copolymer yields a much simpler series of reactions. As shown in Fig. 2.22a-b, the difference spectra from 130 K to 110 K and the difference spectra from 190 K and 170 K show the formation of radical 2 and the loss of a singlet (triplet?) species. This loss of singlet species seems to be connected with the formation of radical 2, and may in fact involve the carboxylic acid radical. This agrees well with the subtraction spectra of 44% and 36% methacrylic acid [Fig. 2.14b] which resembles that of the 77 K methacrylic acid spectrum minus a triplet species. One possible explanation for this could be a transformation of radical 1 into the carboxylic acid radical.

Scheme 2.4

This radical species could then decarboxylate to give the acrylonitrile propagating radical as described earlier. Photobleaching of a sample of 44% methacrylic acid [Fig. 2.24] copolymer showed only a small contribution of radical 4 to the ESR spectrum, and so could not be involved in these transformations to any great extent. Above room temperature [Fig. 2.22d] we begin to see the loss of radical 2. It is interesting to note that there is a

significant amount of methacrylic acid units within the backbone of the polymer, yet there is still no evidence of the characteristic methacrylic acid propagating radical. One would expect to see formation of methacrylic acid propagating radicals due to the increased stability of the tertiary methacrylic acid propagating radical over the secondary acrylonitrile propagating radical. This may be due to some electronic effect of the acrylonitrile unit promoting beta scission, the smaller energy of rotation of the acrylonitrile unit, or some combination of both.

Finally, examination of the subtraction spectra of warm-up experiment of the 75% methacrylic acid completes the picture. As in the two previously described warm-up experiments for 130 K to 150 K [Fig. 2.23a], we see the loss of a singlet species and the formation of radical 2. For 190 K to 210 K [Fig. 2.23b] we see continued formation of radical 2 along with the methacrylic acid propagating radical. The lack of formation of radical 5 at low temperatures supports the possibility of the rate of formation being influenced by the smaller energy of rotation of the acrylonitrile unit. For 250 K to 270 K [Fig. 2.23c] we see the loss of an undefined singlet species, and as in the previous two warm-up experiments, the loss of acrylonitrile propagating radical. Finally, for 310 K to 330 K [Fig. 2.23d] we see the radical 5 and radical 2 decaying.

The warm-up experiments support the mechanisms shown below as being two of the major reactions occurring during the irradiation of methacrylic acid/acrylonitrile copolymers:

Scheme 2.5

The above mechanism is supported by the large amounts of acrylonitrile propagating radical being formed at low temperatures in all of the warm-up experiments. The above mechanism also explains why there is little methacrylic acid propagating radical (radical 5) seen in the polymer samples irradiated at room temperature until there is a high methacrylic acid content. This is due to the fact that that radical 5 will not be present unless there are a significant number of AMM and MMM triads along the copolymer backbone.

Photobleaching of the 44% and 63% MAA [Figs. 2.24 and 2.25] indicate that there is only a small contribution of radical anions to the 77 K ESR spectrum of these copolymers. The 44% MAA copolymer shows a loss of only 6%, and the 63% MAA copolymer only lost 3%. Warming of the 44% MAA copolymer to room temperature after photobleaching shows an additional loss

of 23%. The major radicals being lost are radical 1, and the carboxylic acid radical [Fig. 2.24d]. Again the radical 2 appears to be the major component being formed. Photobleaching also removes the carboxylic acid radical anion (radical 3) from the 63% MAA as seen in Figs. 2.25a-c. It is interesting to note that upon warming, there is a loss of radical 2 and the formation of radical 5 [Fig. 2.25d]. The loss of the acrylonitrile propagating radical seems to account for most of the >56% of the radicals lost upon warming to room temperature.

Conclusion

Although the ESR experiments on the methacrylic acid/acrylonitrile copolymers provide many details about the radiation chemistry of these materials, further study is required to bring our understanding to the stage where this knowledge can be practically exploited. Because of the unusual nature of these copolymers, it was difficult to determine the molecular weight of these copolymers due to their insolubility in common solvents used in GPC. Viscosity experiments would most likely provide the best guide to changes in molecular weight. Based on the radicals seen in the ESR spectra, chain scission is probably the major factor responsible for changes in molecular weight in the irradiated copolymers based on the large concentration of propagating radicals in the ESR spectra. It was also observed that methacrylic acid units are directly responsible for the formation of an increased yield of acrylonitrile propagating radicals. There were many points of interest brought to light which make these copolymers worthy of further examination. Firstly, methacrylic acid/acrylonitrile copolymers are the first reported copolymers that show enhanced radiation sensitivity over their parent homopolymers. This could lead to the development of even more radiation sensitive materials. Polymethacrylic acid is also structurally similar to polymethylmethacrylate which has been shown to be capable of some of the highest resolution in electron beam lithography.^{51,52} However, polymethylmethacrylate is not as sensitive to radiation and the long exposure/raster times needed to obtain good masks have limited its application. The use of some of the copolymers examined in this study could yield similar resolution, with shorter exposure times. Secondly, because the ESR spectrum shows that propagating radicals are among the primary radicals formed, chain scission is probably the dominant reaction. We have also shown that the copolymers containing 60%

to 75% methacrylic acid have very high radical yields, and that these radicals decay readily at room temperature. The disappearance of radicals at room temperature indicates that they are highly reactive and that the main result is chain scission. These properties make the copolymers primary candidates for negative electron beam (UV?) resists. Finally, the solubility of the high methacrylic acid copolymers in methanol and aqueous base makes these materials attractive to silicon chip manufacturers who are trying to eliminate the need for the highly toxic solvents used currently.

Table 2.2 Reaction Conditions and Yields for the Preparation of Methacrylic Acid/Acrylonitrile Copolymers

Sample	Methacrylic Acid	Acrylonitrile	BPO	Time	Yield
63%MAA/37%AN	20ml(0.235mol)	35ml(0.532mol)	0.0256g	120min	2.04g (4.2%)
89%MAA/11%AN	32ml(0.377mol)	12ml(0.182mol)	0.0251g	67min	3.12g (7.4%)

Table 2.3 Distribution of Triad Fractions in Methacrylic Acid/Acrylonitrile Copolymers

Sample	Fractions of M-centered Triads			Fractions of A-centered Triads		
	MMM	AMM and MMA	AMA	MAM	AAM and MAA	AAA
63%MAA/37%AN	0.178	0.478	0.344	0.609	0.264	0.127
89%MAA/11%AN	0.713	0.264	0.039	0.882	0.118	0.000

Fig. 2.1 ^{13}C NMR Spectra Showing the Carbonyl and Nitrile Peaks of Methacrylic Acid/Acrylonitrile Copolymers

Fig. 2.2 The Effect of γ -Rays on the ESR Spectrum of Polyacrylonitrile

Fig. 2.3 The Effect of γ -Rays on the ESR Spectrum of 11% Methacrylic Acid/89% Acrylonitrile Copolymer

Fig. 2.4 The Effect of γ -Rays on the ESR Spectrum of 24% Methacrylic Acid/78% Acrylonitrile Copolymer

Fig. 2.5 The Effect of γ -Rays on the ESR Spectrum of 36% Methacrylic Acid/64% Acrylonitrile Copolymer

Fig. 2.6 The Effect of γ -Rays on the ESR Spectrum of 44% Methacrylic Acid/56% Acrylonitrile Copolymer

Fig. 2.7 The Effect of γ -Rays on the ESR Spectrum of 63% Methacrylic Acid/37% Acrylonitrile Copolymer

Fig. 2.8 The Effect of γ -Rays on the ESR Spectrum of 75% Methacrylic Acid/25% Acrylonitrile Copolymer

Fig. 2.9 The Effect of γ -Rays on the ESR Spectrum of 89% Methacrylic Acid/11% Acrylonitrile Copolymer

Fig. 2.10 The Effect of γ -Rays on the ESR Spectrum of 91% Methacrylic Acid/9% Acrylonitrile Copolymer

Fig. 2.11 The Effect of γ -Rays on the ESR Spectrum of Polymethacrylic Acid

Fig. 2.12 Effect of Composition on $G[\text{radical}]$ in Methacrylic Acid/Acrylonitrile Copolymers

Fig. 2.13 Simulated ESR Spectra of Radical Species Found in Irradiated Polyacrylonitrile and Polymethacrylic Acid

Fig. 2.14 Difference ESR Spectra of Methacrylic Acid/Acrylonitrile Copolymers Irradiated at 77K

Fig. 2.15 Difference ESR Spectra of Methacrylic Acid/Acrylonitrile Copolymers Irradiated at 303K

Fig. 2.16 Effect of Composition on the Glass Transition Temperature of Methacrylic Acid/Acrylonitrile Copolymers

▼ literature values⁵³⁻⁵⁴
 ○ experimentally determined

Fig. 2.17 Effect of Temperature on the Radical Yield in Methacrylic Acid/Acrylonitrile Copolymers

Fig. 2.18 Effect of Temperature on the ESR Spectrum of 24% Methacrylic Acid/76% Acrylonitrile Irradiated at 77 K

Fig. 2.19 Effect of Temperature on the ESR Spectrum of 44% Methacrylic Acid/56% Acrylonitrile Irradiated at 77 K

Fig. 2.20 Effect of Temperature on the ESR Spectrum of 75% Methacrylic Acid/25% Acrylonitrile Irradiated at 77 K

Fig. 2.21 Difference ESR Spectra from the Warmup of 24% Methacrylic Acid/76% Acrylonitrile Copolymer from 110 K to 330 K

Fig. 2.22 Difference ESR Spectra from the Warmup of 44% Methacrylic Acid/56% Acrylonitrile Copolymer from 110 K to 330 K

Fig. 2.23 Difference ESR Spectra from the Warmup of 75% Methacrylic Acid/25%Acrylonitrile Copolymer from 110 K to 330 K

Fig. 2.24 Difference ESR Spectra from the Photobleaching of 44% Methacrylic Acid/56% Acrylonitrile Irradiated at 77 K

Fig. 2.25 Difference ESR Spectra from the Photobleaching of 63% Methacrylic Acid/37% Acrylonitrile Irradiated at 77 K.

Appendix A: Fricke Dosimetry

Calibration of the radiation source was accomplished using Fricke dosimetry. This was done using the standard procedure.^{56,57} The Fricke reagent was prepared by combining the following reagents to a 1000 mL volumetric flask: 600 mL of distilled water, 22 mL of 98% sulfuric acid (AR grade), 0.5605 g of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, and 0.608 g of NaCl. After mixing the solution was allowed to cool before being diluted to the final volume of 1000 mL with distilled water. The Fricke reagent was stored in the dark, and wrapped in foil until use. To ensure proper performance, the reagent was used within a week of preparation. Aliquots of Fricke reagent were transferred to stoppered test tubes. Each aliquot was then separately irradiated for 5 to 10 minutes. The sample holders used for the Fricke dosimetry were designed to position the test tubes in the same position in the source as were the ESR tubes. For room temperature simulation, samples were placed in the same aluminum container that was used to hold the ESR tubes. For 77 K simulation, the samples were placed in the same dewar that was used to hold the ESR tubes and a separate dosimetry experiment conducted to account for the variance in the apparatus. Since the use of liquid nitrogen in the dewar would change the temperature, and thus the reaction kinetics of the dosimetry, a 63.6/36.4 (v/v) mixture of acetone/water, which was determined to have the same molar absorption coefficient as liquid nitrogen,⁵⁸ was used as a substitute liquid, and the dosimetry conducted at room temperature. After exposure, the sample was transferred to a 1 cm quartz cuvet and the absorbance measured at 304nm with a UV/Vis spectrophotometer using unirradiated Fricke reagent as a reference. Given the molar absorptivity of (extinction coefficient) of $\epsilon = 2193 \text{ L/mol/cm}$ at

298 K and the temperature in the spectrophotometer (T_2) measured to be 295 K, the change in the molar absorptivity was calculated using the equation:⁵⁹

$$\epsilon_2 = 2193 [1 + 0.007(T_2 - 298)] = 2146 \quad [A.1]$$

The molar concentration of Fe^{+3} could then be calculated from the absorbance using the formula:⁶⁰

$$[\text{Fe}^{+3}] = \text{abs}/\epsilon_2 = \text{mol/L} \quad [A.2]$$

By plotting the concentration of $[\text{Fe}^{+3}]$ against exposure time (in seconds), the rate of formation $d[\text{Fe}^{+3}]/dt$ was determined. Given that $G[\text{Fe}^{+3}]$ when using ^{60}Co γ -rays is 15.5 and the density of Fricke reagent is 1.024 Kg/L, the dose rate (in kGy/hr) could be calculated using the equation:⁶⁰

$$D_0 = \frac{d[\text{Fe}^{+3}]/dt(3600\text{sec/hr})(6.02 \times 10^{23} \text{atoms/mol})(16 \times 10^{-18} \text{J/Kg/100eV})}{(1.024 \text{Kg/L})(15.5 \text{atoms/100eV})} \quad [A.3]$$

On September 20, 1990, the dose rate was determined to be 0.569 kGy/hr using a holder which kept the vials of Fricke reagent in the same position as the ESR tubes would be placed in the gammacell. On September 24, 1990, the dose rate was determined to be 0.483 kGy/hr under simulated liquid nitrogen conditions.

Fig. A.1 Concentration of Iron(III) in Fricke Solution with Length of Exposure to 1.25MeV γ -rays

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