

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Oligomers and Polymers of Polyethers and Polyformals

A. S. Hay^a; F. J. Williams^a; H. M. Relies^a; B. M. Boulette^a

^a Corporate Research & Development, General Electric Co., New York

To cite this Article Hay, A. S. , Williams, F. J. , Relies, H. M. and Boulette, B. M.(1984) 'Oligomers and Polymers of Polyethers and Polyformals', *Journal of Macromolecular Science, Part A*, 21: 8, 1065 – 1079

To link to this Article: DOI: 10.1080/00222338408056592

URL: <http://dx.doi.org/10.1080/00222338408056592>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Oligomers and Polymers of Polyethers and Polyformals

A.S. Hay, F.J. Williams, H.M. Relles, and B.M. Boulette

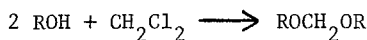
General Electric Co., Corporate Research & Development
P.O. Box 8, Schenectady, New York 12301

ABSTRACT

Linear high molecular weight aromatic polyformals are readily obtained from biphenols and excess methylene chloride with solid sodium hydroxide or potassium hydroxide in the presence of a phase transfer catalyst or an aprotic dipolar solvent. By control of the stoichiometry bifunctional oligomers can be obtained which can subsequently be incorporated into a variety of block copolymers.

INTRODUCTION

Dehmlow and Schmidt⁽¹⁾ found that methylene chloride would react with phenols or alcohols in the presence of solid KOH and a phase transfer catalyst (e.g. methyltricaprylyl ammonium chloride) to yield formals (I; R=Aryl or Alkyl) as products. Yields of 80-97% were



I

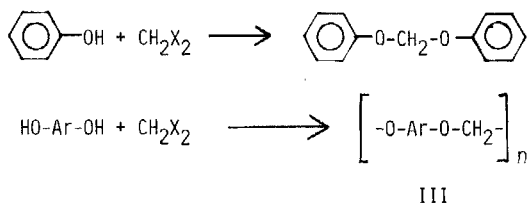
obtained at room temperature when the reactions were run overnight in methylene chloride as solvent. The intermediate chloroethers (II).



II

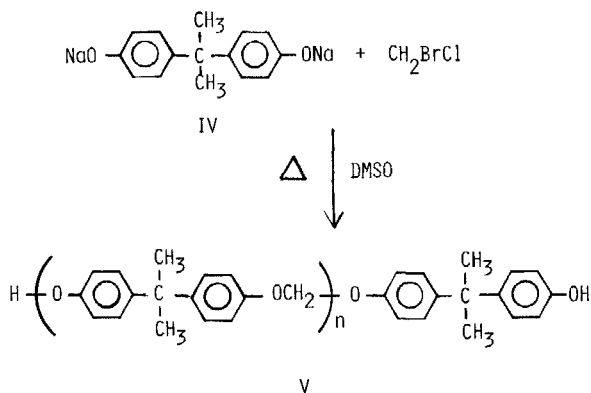
were apparently present only in very small amounts early in the reaction which indicates that they are considerably more reactive toward nucleophilic substitution than methylene chloride and also explains why methylene chloride can be used as both reactant and solvent. Alcohols are considerably less reactive, however, when the reactions are carried out at the temperature of reflux for extended times, good yields of the formals are obtained.

Earlier, McKillop, Fiaud & Hug,⁽²⁾ in attempting to alkylate *p*-*t*-butylphenol with benzyl chloride under phase transfer conditions had unexpectedly obtained as the major product di-*p*-*t*-butylphenoxymethane. The expected benzyl ether was obtained only if stoichiometric amounts of the quaternary ammonium salt were used.

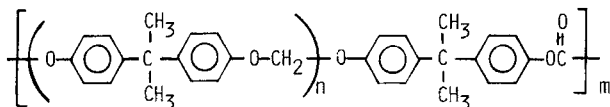


It appeared probable that by the use of bisphenols, under the conditions described by Dehmlow, linear aromatic polyformals (III) could be synthesized.

Low molecular weight aromatic polyformals have previously been synthesized by Barclay⁽³⁾.



He found that oligomers (V: $\text{dp} \sim 17$) were obtained when the disodium salt of bisphenol-A (IV) was reacted with bromochloromethane in DMSO solvent at elevated temperatures (up to 150°C). The oligomers are hydroxyl terminated and high molecular weight formal carbonate copolymers (VI) can be obtained by reaction with phosgene and base.

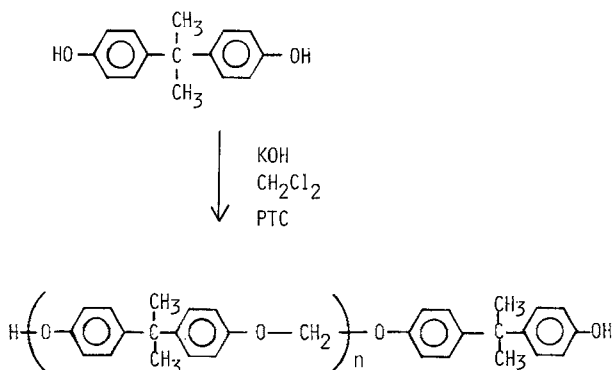


VI

Polymerization of Bisphenol-A with Methylene Chloride

When bisphenol-A is reacted with methylene chloride and excess potassium hydroxide pellets in the presence of monomethyltricaprylyl ammonium chloride (Aliquat 336) in methylene chloride as solvent a thick, pasty, precipitate of the dipotassium salt is first obtained which gradually disappears over an 18 hour period leaving a viscous solution containing a precipitate of potassium chloride and excess potassium hydroxide. A 49% yield of polymer (VII), $[\eta] = 0.31$ dec./g in chloroform at 25°C , is isolated by precipitation into methanol⁽⁴⁾.

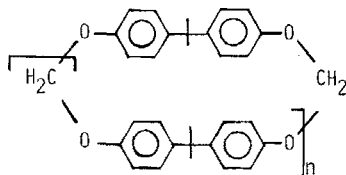
The structure of the polymer is confirmed by Proton and ^{13}C -NMR.



VII

In Table I we see that by raising the temperature to 35°C somewhat higher yields of a higher molecular weight polymer are formed. When a mixed solvent of methylene chloride and chlorobenzene is used the reaction can conveniently be performed at 75°C and much higher yields are obtained. If even higher temperatures are used lower yields and lower molecular weight polymers are obtained presumably because of decomposition of the phase transfer catalyst. If a dipolar aprotic solvent such as N-methylpyrrolidone as a cosolvent with methylene chloride is used in the absence of a phase transfer catalyst the reaction is much faster and high yields are obtained. The optimum reaction temperature is about 70°C. In these cases it is also necessary to add a monofunctional phenol as a chain stopper to limit the molecular weight obtained. Similar results are obtained with sodium hydroxide.

When these isolated polymers are compression molded the molded pieces are hazy indicating the presence of some crystalline material. Subsequent analysis of the mother liquors obtained after precipitation of the polymer in methanol indicated the presence of low molecular weight products which were identified by mass spectrometry and ^{13}C -NMR as principally the cyclic dimer and trimer (VIII;n=1,2).



VIII

By gradient elution liquid chromatography all the cyclic oligomers can be identified (Fig. 1) and if a chromatogram of a reaction mixture is taken in the early stages of a polymerization it shows, in addition, the presence of linear oligomers and cyclic oligomers (Fig. 2).

TABLE I
Polymerization of Bisphenol-A

<u>PTC</u>	<u>Base</u>	<u>Solvent</u>	<u>Temperature</u> (°C)	<u>Time</u> (hrs)	<u>Yield</u> %	<u>ln</u> (dec/g)
Aliquat 336	KOH	CH ₂ Cl ₂	25	18	49	0.31
Aliquat 336	KOH	CH ₂ Cl ₂	35	21	70	0.60
Aliquat 336	NaOH	CH ₂ Cl ₂ /Cl ₂	75	4	93	0.57
-	NaOH	CH ₂ Cl ₂ /N-Methyl- pyrrolidine	70	1	78	0.58

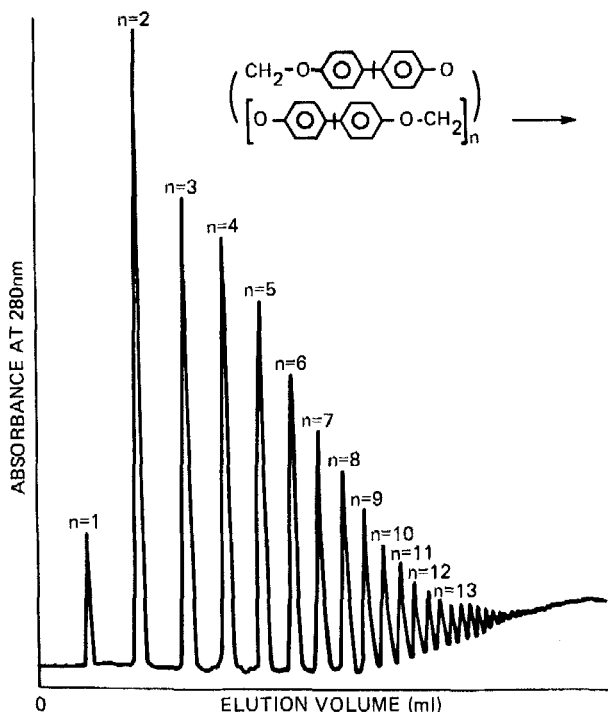


Fig. 1

Under the conditions of the polymerization reaction the formal linkage has been shown to be stable hence the cyclic oligomers that are formed initially persist. The initial formation of the insoluble disodium or dipotassium salts apparently creates essentially the conditions for a high dilution reaction which favors cyclic formation. Higher temperature, higher concentration of phase transfer catalyst or the use of a more polar solvent minimizes, but does not eliminate, the formation of cyclic oligomers.

The properties of the polyformal of bisphenol-A are shown in Table II.

Compression or injection molded pieces of the polymer are tough and transparent, comparable in many properties to the corresponding polycarbonate but with a much lower glass transition temperature.

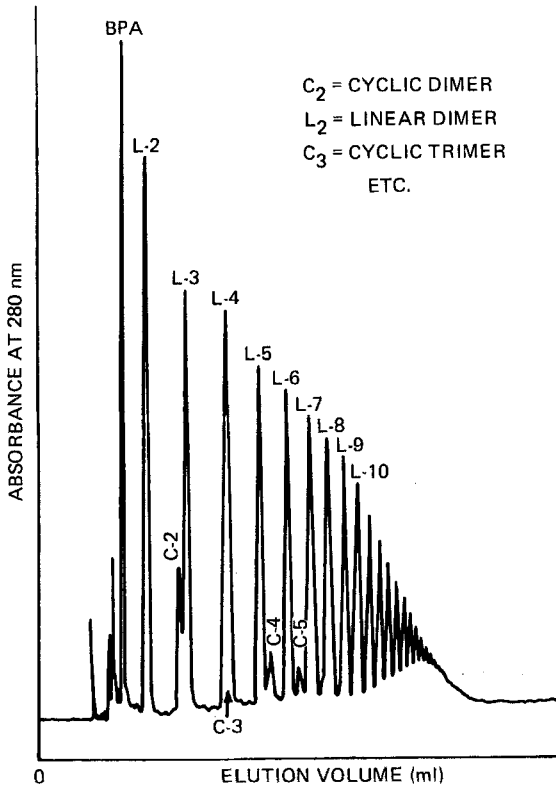


Fig. 2

TABLE II
 BPA POLYCARBONATE VS. BPA POLYFORMAL

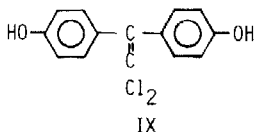
	<u>Polyformal</u>	<u>Polycarbonate</u>
Specific Gravity (g/cc)	1.10	1.20
T _g (°C)	94	149
Oxygen Index	20	27
Yield Stress (psi)	7100	9400
Flexural Modulus (psi x 10 ³)	370	335
Flexural Strength (psi x 10 ³)	12	14.4
% Elongation	80	110
Gardner Impact (ft lbs)	>320	>320
Notched Izod Impact (ft lbs/in notch)	1	16

Synthesis of Other Polyformals

A large number of other polyformals have been synthesized (Table III) and in general the glass transition temperatures are 40–60°C lower than the corresponding polycarbonate. In the preparation of polymers from less reactive bisphenols, such as 4,4'-dihydroxydiphenylsulfone, the use of methylene bromide rather than methylene chloride is advantageous.

The influence of ring substituents on the properties of the polyformals was also studied. The introduction of one methyl substituent (Table IV) on the aromatic ring has little effect on the glass transition temperature and the introduction of two substituents in two cases gives a modest increase in T_g and in one case a modest decrease in T_g . By contrast, the polycarbonate from the tetramethyl derivative of BPA has a T_g of 203°C, an increase of over 50°C above that of the unsubstituted polymer.

The polycarbonate prepared from 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (IX) has properties very similar to BPA polycarbonate



except that it has a very high oxygen index of 57 and is an excellent char former. The monomer is prepared by acid-catalyzed condensation of chloral with phenol and subsequent dehydrohalogenation of the intermediate bisphenol (X).

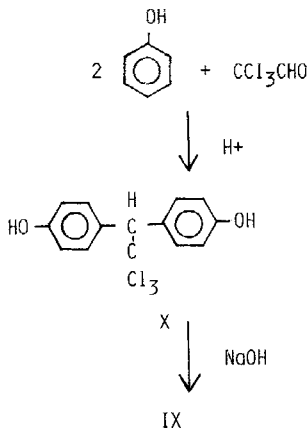


TABLE III
 Aromatic Polyformals


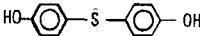
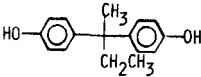
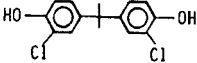
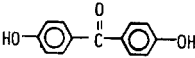
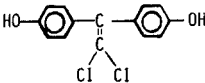
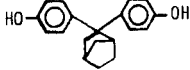
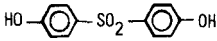
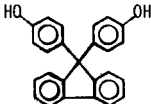
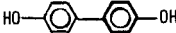
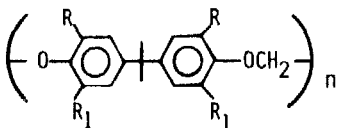
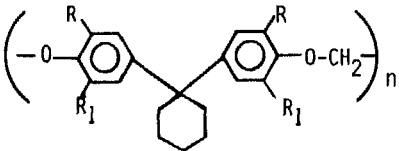
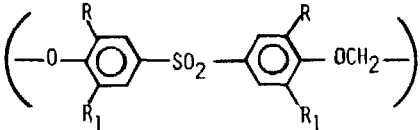
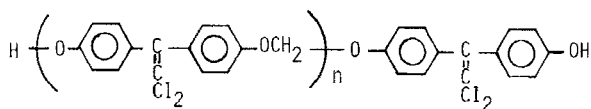
<u>Bisphenol</u>	<u>IV(dl/g)</u>	<u>T_g⁰C (T_m⁰C)</u> <u>Polyformal</u>
	-	41 (200)
	.71	63 (164)
	1.48	87
	0.47	106
	0.47	116
	0.48	120
	-	136 (250)
	0.75	179
	0.64	218
	-	(324)

TABLE IV
Substituent Effects on Polyformals

	<u>R</u>	<u>R₁</u>	<u>T_g^oC</u>
	H	H	93
	CH ₃	H	90
	CH ₃	CH ₃	121
	H	H	107
	CH ₃	H	105
	CH ₃	CH ₃	136
	H	H	179
	CH ₃	CH ₃	169

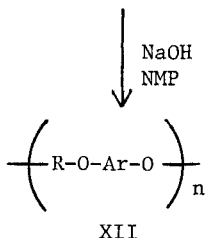
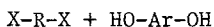
The polyformal XI can be prepared from IX or from the intermediate bisphenol X by using excess base to carry out the dehydrohalogenation simultaneously. The polymer obtained has $T_g=122^\circ\text{C}$ and an oxygen index of 37. Random 50/50 copolymers with BPA or block copolymers prepared by first forming an oligomer, XI, and subsequently coreacting with an equivalent amount of BPA both showed single glass transition temperature intermediate between those of the two homopolymers.



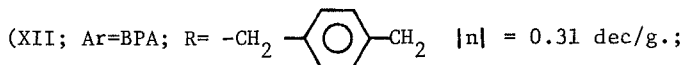
XI

Polyethers and Polyacetals

The reaction has been extended to the synthesis of polyethers and polyacetals (XII) by replacing the methylene chloride with other dihalides.



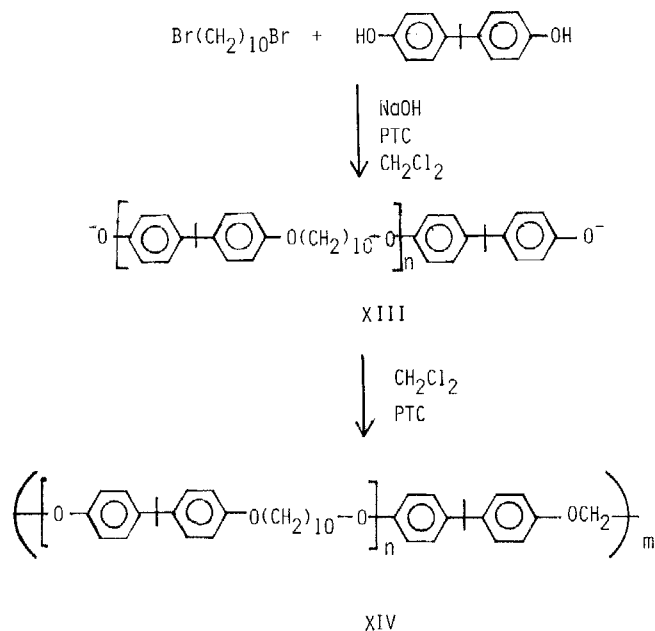
In all of these cases, since the initial dihalide has the same reactivity as the once reacted intermediate, it becomes important to carefully control the stoichiometry if a high molecular weight linear polymer is to be synthesized. With α α' -dichloro p-xylene and bisphenol-A a polyether



T_g , 89°C) is obtained which is insoluble in chloroform but soluble in hot N-methylpyrrolidone. From benzal bromide a polyacetal (XII; Ar=BPA; R= \emptyset CH; T_g , 103°C; $|n| = 0.26 \text{ dec./g}$) is formed.

Copolymers

If reactive dihaloalkanes, e.g. 1,10-dibromodecane, are used the reaction can be carried out with excess BPA in methylene chloride solution so that the initially formed oligomer, XIII, then reacts with methylene chloride to give a high molecular weight linear polymer XIV containing ether and formal linkages. A polymer prepared in this fashion with a 2:1 ratio of BPA to 1,10-dibromodecane has a T_g of 41°C and is a rubbery material.



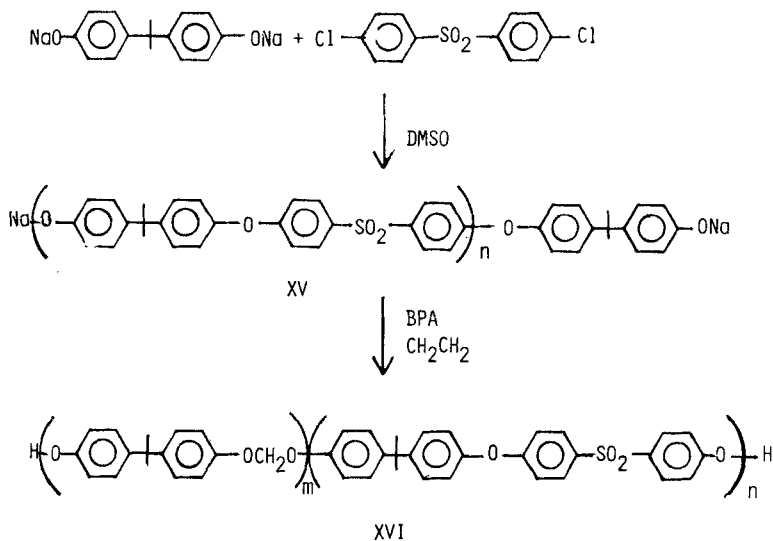
The dihalides listed in Table V were used without success in the synthesis of high molecular weight polymers.

A similar procedure has been used to produce polyethersulfone-formals. Polysulfone oligomers (XV) can first be synthesized by reaction of excess of the disodium salt of BPA with 4,4-dichloro-

TABLE V
Dihalides Which Do Not Produce Polymers

Dichloroacetic Acid
 α, α' Dichloroacetophenone
 1,1-Dichloroethane
 2,2-Dichloroethanol
 1,1-Dichloro-2,2-diethoxyethane
 α, α' -Dichloromethylether
 Methyl dichloroacetate
 1,2-Dibromoethane

diphenylsulfone in dimethylsulfoxide. These hydroxy terminated oligomers can then be converted to high molecular weight polymers by reaction with methylene chloride or to block copolymers (XVI) by coreaction with BPA and methylene chloride.



Oligomeric BPA-Polyformals can be conveniently prepared by controlling the amount of base added to the reaction mixture (Table (VI)).

In all cases a few percent of the NaOH is lost by hydrolytic side reactions.

TABLE VI
Oligomeric BPA-Polyformals

<u>Moles NaOH</u> <u>Moles BPA</u>	<u>% Yield</u>	<u>[n]</u> <u>(dec/g, CHCl₃)</u>	<u>\bar{M}_n</u> <u>(G.P.C.)</u>
1.97	73	0.14	6,120
2.00	73	0.15	5,210
2.04	75	0.17	8,360
2.10	81	0.27	11,500

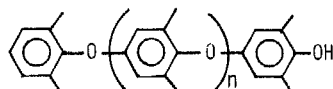
TABLE VII
Block Copolyformal-carbonates

Polyformal Oligomer \bar{M}_n	Weight Ratio Oligomer:BPA	% Yield	$[\eta]$ (dec/g;CHCl ₂)	T _g (°C)
6000	75:25	91	0.82	106
5200	50:50	94	0.52	112
6000	50:50	90	0.66	120
6000	25:75	85	1.06	130

These oligomers can then be copolymerized with BPA and phosgene to yield copolyformal-carbonates. (Table VII)

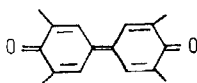
In all cases a single glass temperature is observed which is in between that of the homopolymers. Blends of the homopolymers are however immiscible since the glass temperatures of the individual homopolymers are retained and compression molded samples of the blends are not transparent.

Polyphenylene oxides (XVII) prepared by oxidative coupling of 2,6-dimethylphenol are terminated on one end by hydroxyl.

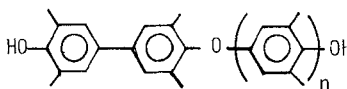


XVII

White⁽⁵⁾ has shown that by equilibration with 3,3',5,5'-tetramethyl-diphenoquinone (XVIII) bifunctional polyphenylene oxides (XIX) can be prepared.



XVIII



XIX

When these oligomers are coupled with polyformal oligomers by means of isophthaloyl/chloride and base under phase transfer conditions block copolymers are obtained⁽⁶⁾. In this case the copolymers give transparent films on compression molding which show two distinct glass transition temperatures. A blend of the two homopolymers is not transparent and also shows two glass transition temperatures.

REFERENCES

1. E.V. Dehmloew and J. Schmidt, *Tet. Letters* 2, 95 (1976)
2. A. McKillop, J.C. Fiaud and R.P. Hug, *Tetrahedron* 30, 1379 (1974)
3. R. Barclay, U.S. Patent 3,069,386 (Dec. 18, 1962).
4. A.S. Hay, F.J. Williams, H.M. Relles, B.M. Boulette, P.E. Donahue and D.S. Johnson, *J. Polym. Sci., Letters* 21, 449 (1983); A.S. Hay, U.S. Patent 4,374,974 (1983); A.S. Hay, U.S. Patent 4,254,254 (1981); G.R. Loucks and F.J. Williams, U.S. Patent 4,136,087 (1979); D.S. Johnson, U.S. Patent 4,163,833 (1979); H.M. Relles and D.S. Johnson, U.S. Patent 4,210,731 (1980).
5. D.M. White, *J. Polym. Sci. Pol. Chem. Ed.* 19, 1367 (1981).
6. D.M. White, U.S. Patent 4,356,290 (1982); D.M. White and G.R. Loucks, U.S. Patent 4,340,696 (1982).