(11) Anderson, R. A.; Reid, R. F.; Soutar, I. *Eur. Polym. J.* **1980**, *16*, 945.
(12) David, C.; Baeyens-Volant, D.; Piens, M. *Eur. Polym. J.* **1980**, *16*, 413.
(13) Hirayama, F. J. *J. Chem. Phys.* **1965**, *42*, 3163.
(14) Houben, J. L.; Natucci, B.; Solaro, R.; Colella, O.; Chiellini, E. *Polymer* **1978**, *19*, 811.
(15) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2082.
(16) Ishii, T.; Handa, T.; Matsunaga, S. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 811.
(17) Pino, P.; Ciardelli, F.; Zandomeneghi, M. *Annu. Rev. Phys. Chem.* **1970**, *21*, 561.
(18) Ciardelli, F.; Chiellini, E.; Carlini, C.; Pieroni, O.; Salvadori, P.; Menicagli, R. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 62*, 143.
(19) Galli, G.; Solaro, R.; Chiellini, E.; Ledwith, A. *Macromolecules* **1983**, *16*, 497.
(20) Perrin, F. *Ann. Phys.* **1929**, *12*, 169.
(21) Hug, W.; Ciardelli, F.; Tinoco, I., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 3407.
(22) Ciardelli, F.; Aglietto, M.; Carlini, C.; Chiellini, E.; Solaro, R. *Pure Appl. Chem.* **1982**, *54*, 521.
(23) Chiellini, E.; Solaro, R.; Colella, O.; Ledwith, A. *Eur. Polym. J.* **1978**, *14*, 489.
(24) Chiellini, E.; Solaro, R.; Galli, G.; Ledwith, A. *Macromolecules* **1980**, *13*, 1654.
(25) Galli, G.; Solaro, R.; Chiellini, E.; Ledwith, A. *Polymer* **1981**, *22*, 1088.
(26) Carlini, C.; Chiellini, E. *Makromol. Chem.* **1975**, *176*, 519.
(27) Majumdar, R. N.; Carlini, C. *Makromol. Chem.* **1980**, *181*, 201.
(28) Majumdar, R. N.; Carlini, C.; Bertucci, C. *Makromol. Chem.*, **1982**, *183*, 2047.
(29) Altomare, A.; Carlini, C.; Solaro, R. *Polymer* **1982**, *23*, 1355.
(30) Majumdar, R. N.; Carlini, C.; Rosato, N.; Houben, J. L. *Polymer* **1980**, *21*, 941.
(31) Story, V. M.; Canty, G. *J. Natl. Bur. Stand. A, Phys. Chem.* **1964**, *68A*, 165.
(32) David, C.; Baeyens-Volant, D.; Geuskens, G. *Eur. Polym. J.* **1976**, *12*, 71.

Far-Ultraviolet Circular Dichroism Spectra of Isotactic Optically Active Poly(alkyl vinyl ethers) and Their Low Molecular Weight Models

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ABSTRACT: Vacuum-UV circular dichroism (CD) (210–140 nm) spectra of optically active poly(alkyl vinyl ethers) are reported and compared with those of low molecular weight analogues. In spite of the ordered structure of the macromolecules, no particular CD feature connected with the polymer conformation is evident. However, the CD is sensitive to even subtle differences in the isotacticity degree of the polymeric samples.

Introduction

The stereochemical properties of isotactic chiral synthetic polymers have been widely investigated by chiroptical techniques, and the relationship between the conformation in solution of the macromolecules and their optical activity has been established by experimental and theoretical studies.[1] As far as optically active poly(alkyl vinyl ethers) are concerned, the aforementioned relationship has not been properly investigated because of the instrumental difficulty in measuring far-UV optical rotatory dispersion (ORD) and circular dichroism (CD) spectra. In fact, the chiroptical properties of poly(alkyl vinyl ethers) were investigated down to 185 nm and only the lowest energy band related to the ethereal chromophore was detected.[2] The same occurred for optically active poly(oxiranes), in which the ethereal oxygen is located in the main chain.[3] The data reported on the chiroptical properties of the poly(alkyl vinyl ethers) indicate that in solution the macromolecules assume a helical conformation with a predominant screw sense, as proposed for poly(α-olefins).[4]

More recently, the CD of the ether chromophore was reconsidered, thanks to the availability of special far-UV CD spectrometers. Some papers appeared in the literature concerning the far-UV CD of poly[(*R*)-oxypropylene][5] and of low molecular weight ethers.[6-8] Therefore, it appeared interesting to investigate the vacuum-ultraviolet spectral region also for the poly(alkyl vinyl ethers), with the aim of more properly establishing the relationship between optical activity and conformation in solution.

Experimental Section

Synthesis of Polymers. Poly(menthyl vinyl ether) (IA–C) samples were obtained by polymerization of (−)-menthyl vinyl ether by using different catalytic systems and experimental conditions that have been described elsewhere.[9,10] The polymers were purified by several reprecipitations with methanol from hydrocarbon or chloroform solutions (Table I). Poly[(*S*)-1-methylheptyl vinyl ether] (IIA,B) samples were obtained by polymerization of the corresponding monomer in the presence of a catalyst based on the $Al(O\text{-}i\text{-}C_3H_7)_3/H_2SO_4$ system and $BF_3{\cdot}OEt_2$, respectively, according to the procedure previously described.[10]

The model compounds for the isolated chromophore, (−)-menthyl ethyl ether and (−)-(*S*)-1-methylheptyl ethyl ether, were prepared by hydrogenation of the corresponding vinyl ethers in the presence of Raney Ni according to a procedure described elsewhere.[11]

^{13}C NMR Spectra. NMR spectra were recorded on a Bruker HF-90 and the evaluation of the isotacticity degree was done for polymer I samples on the basis of the signal at 48.5 ppm (Me_4Si),[12] whereas for polymer II samples no definitive attribution has been so far performed.

CD Measurements. CD spectra were recorded with a vacuum-ultraviolet spectrometer[13] by using standard cylindrical quartz cells of 50- and 100-μm path length for the bulk of the measurements. Sandwich-type cells with aluminum foil spacers were

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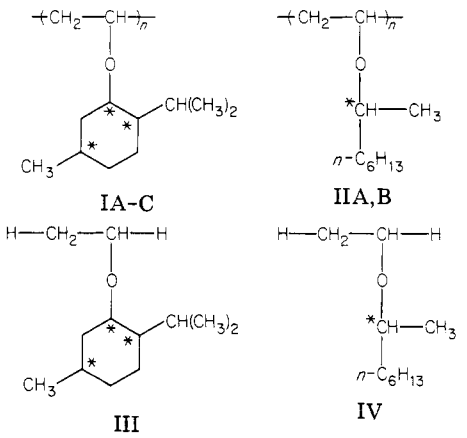
Table I
Physical Properties of the Optically Active Poly(alkyl vinyl ethers) and Low Molecular Weight Structural Models

sample	poly(alkyl vinyl ethers)						model compounds	
	polymerization conditions							
	monomer							
	structure	$[\alpha]^{25}_D$, deg	catalyst	$[\alpha]^{25}_D$, deg	$[\eta]$, dL/g	ID[c]	type	$[\alpha]^{25}_D$, deg
IA	(−)-menthyl vinyl ether[a]	−73.6 (neat)	$C_2H_7SbCl_6$	−196	0.34	75	(−)-menthyl ethyl ether	−89.0 ($CHCl_3$)
IB			$BF_3 \cdot OEt_2$	−208	0.45	75		
IC			$AlCl_2Et$	−208	0.56	80		
IIA	(−)-(*S*)-1-methylheptyl vinyl ether[b]	−0.84	$BF_3 \cdot OEt_2$	+68.2		*d*	(*S*)-1-methylheptyl ethyl ether	−10.3 ($CHCl_3$)
IIB			$Al(O\text{-}i\text{-}C_3H_7)_3$-$H_2SO_4$	+82.7		*e*		

[a] Optical purity 100%. [b] Optical purity 90.9%. [c] Isotactic degree; determined by NMR. [d] Partially isotactic. [e] Semicrystalline isotactic.

Chart I



also used to further extend the spectra into the vacuum UV. Suprasil windows from Amersil Inc. were used for measurements above 160 nm and CaF_2 windows from Frank Cook Inc. for measurements below 160 nm. Pentane, isooctane, dodecane, and perfluorohexane solutions were used ($C = 1.3 \times 10^{-2}$ mol/L). Films of the polymers were obtained by slow evaporation of the solvent from a dilute ($C = 1 \times 10^{-2}$ mol/L) solution of the samples dissolved in hydrocarbons. All the films were tested to exclude any orientation dependence of the CD signals. In all cases the total optical density of the cell, solvent, and sample was kept below 1.0. The spectral slit width was a constant 1.6 nm.

Results and Discussion

In the present paper the CD spectra recorded for solid film and solution are reported for three samples of poly[(−)-menthyl vinyl ether] (IA–C; Chart I) prepared by different catalytic systems and characterized by a comparable isotacticity degree (75–80% isotactic dyads). Two different samples of poly[(*S*)-1-methylheptyl vinyl ether] (IIA,B) prepared in the presence of two different catalytic systems, leading, respectively, to partially isotactic (IIA) and isotactic semicrystalline (IIB) poly(alkyl vinyl ether),[10] are also studied. The investigation extended the CD down to 140 nm, and the measured spectra are compared with those of the corresponding model chromophores, (−)-menthyl ethyl ether (III) and (*S*)-1-methylheptyl ethyl ether (IV). In Table I are collected the data relevant to the characteristics of the polymer samples investigated and the corresponding structural models.

The UV spectra of the poly(alkyl vinyl ethers) and the model ethers do not show any significant difference in the profile of the absorption that steeply increases in the 180–150-nm range (not shown).

CD spectra of polymers I and II were recorded either as solid films or in hydrocarbon solution, whereas the structural models, III and IV, were analyzed in hydrocarbon or perfluorohexane solution. Due to the insolubility of the polymers in fluorinated hydrocarbons, their CD spectra in solution were limited by the absorption of the hydrocarbon solvents to 170 nm as the shortest wavelength. The CD spectra measured for the polymers in hydrocarbon solution show dichroic bands at the same energy as the bands measured for the films, even though the intensities are rather different.

The comparison between the polymers and the corresponding structural models shows a similarity between their CD spectra as far as the number and the sign of the bands are concerned (Figures 1 and 2). On the contrary,

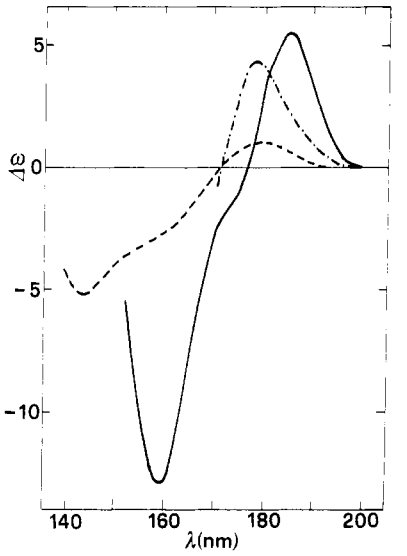


Figure 1. CD of IA in pentane (−·−) and as a film (−−−) and of III in perfluorohexane solution (—).

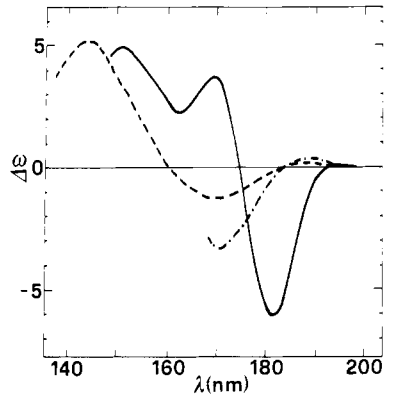


Figure 2. CD of IIA in pentane (−·−) and as a film (−−−) and of IV in perfluorohexane solution (—).

Table II
CD Characterization of Poly[(−)-menthyl vinyl ether] (I), Poly[(S)-1-methylheptyl vinyl ether] (II), and the Corresponding Structural Models (−)-Menthyl Ethyl Ether (III) and (S)-1-Methylheptyl Ethyl Ether (IV)

sample	solvent	λ_{max}, nm	$\Delta\epsilon_{max}$	λ_{max}, nm	$\Delta\epsilon_{max}$	λ_{max}, nm	$\Delta\epsilon_{max}$	λ_{max}, nm	$\Delta\epsilon_{max}$
IA	pentane			179	+3.4				
	film			180	+0.7	158 (sh)	−2.4	144	−4.2
IB	pentane			178	+3.6				
	film			180	+0.9	158 (sh)	−2.7	144	−5.0
IC	pentane			177	+3.9				
	film			180	+1.0	158 (sh)	−2.8	144	−5.1
IIA	pentane	188	+0.19	170	−2.9				
	film	188	+0.03	170	−1.2	155 (sh)	+1.5	143	+4.2
IIB	pentane	187	+0.35	170	−3.6				
	film	188	+0.10	170	−1.3	155 (sh)	+2.0	143	+5.2
III	pentane			185	+6.8				
	perfluorohexane			184	+5.5	171 (sh)	−2.0	159	−12.9
IV	pentane	195	+0.02	182	−7.1	170	+4.4		
	perfluorohexane	194	+0.02	181	−6.1	169	+3.7	151	+5.0

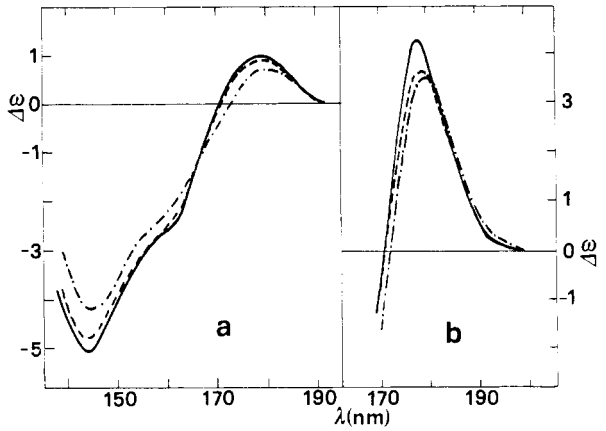


Figure 3. CD dependence of I on the tacticity degree. (a) CD as a film: (-·-) IA; (-··-) IB; (—) IC. (b) CD in pentane solution: (-·-) IA; (-··-) IB; (—) IC.

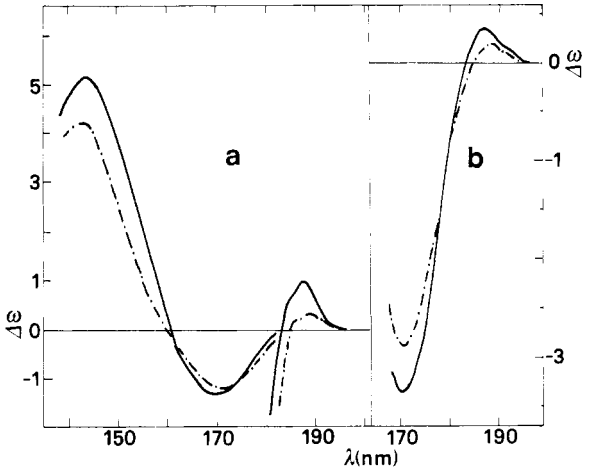


Figure 4. CD dependence of II on the tacticity degree. (a) CD as a film: (—) IIA; (-·-) IIB. (b) CD in pentane solution: (—) IIA; (-·-) IIB.

a noticeable difference is recognizable in the position and relative intensity of the bands (Figures 1 and 2). The lowest energy band in III is centered at about 185 nm, but it is blue shifted nearly 5 nm in the corresponding polymer (I). This band has been assigned to a Rydberg-type transition of a nonbonding electron of the oxygen in aliphatic ether.[6,14] The same band is centered at 181 nm in IV, whereas a blue shift of 10 nm is observed in II. The intensity of this band is higher in the low molecular weight models than in the corresponding polymers.

A very low intensity band is also present in the CD spectra of II and IV at about 190 nm, which has been identified as a "hot band" because of its marked enhancement with increasing temperature.[15] Within the limitations of the presented data, no clear evidence of exciton coupling interactions among the side-chain chromophores can be put forward, in contrast to what is observed in the case of other synthetic[16] and natural polymers.[17] The high perturbability of the ethereal chromophore by environmental effects might cause the bands in the structural models to blue shift in the polymers. However, no significant information can be drawn from the CD on the conformation of the macromolecules in solution.

Even if the general trend of the spectra is the same in solution and in the solid state, the poor reproducibility of the latter does not allow us to draw any definitive conclusion on the relationship between the intensity of the CD bands and the degree of stereoregularity. A more reliable feature can be obtained from measurements carried out in solution, which show that a higher dichroic absorption is obtained for polymeric samples having a higher isotacticity degree (Table II) as determined by NMR on a quantitative basis in the case of samples I and on a qualitative basis for samples II (Table I). In this connection it is worth mentioning that sample IA, prepared under free ion cationic conditions, shows chiroptical properties and tacticity degree not appreciably different from those of samples IB and IC prepared under conventional stereospecific polymerization conditions, thus clearly confirming the peculiar behavior of (−)-menthyl vinyl ether in the cationic polymerization.[9]

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Registry No. I, 26099-46-7; II, 84303-70-8; III, 13947-22-3; IV, 36978-30-0.

References and Notes

(1) Ciardelli, F.; Carlini, C.; Chiellini, E.; Salvadori, P.; Lardicci, L.; Menicagli, R.; Bertucci, C. "Preparation and Properties of Stereoregular Polymers"; Lenz, R. W.; Ciardelli, F., Eds; D. Reidel Publishing Co.: Dordrecth, 1979; pp 353–368 and references therein.
(2) Pino, P.; Salvadori, P.; Lorenzi, G. P.; Chiellini, E.; Lardicci, L.; Consiglio, G.; Bonsignori, O.; Lepri, L. *Chim. Ind. (Milan)* **1973**, *55*, 182.
(3) Chiellini, E.; Salvadori, P.; Osgan, M.; Pino, P. *J. Polym. Sci., Part A-1* **1970**, *8*, 1589.
(4) Pino, P. *Adv. Polym. Sci.* **1965**, *4*, 393.
(5) Hirano, T.; Sato, A.; Tsuruta, T.; Johnson, W. C., Jr. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1601.
(6) Sharman, E. H.; Schnepp, O.; Salvadori, P.; Bertucci, C.; Lardicci, L. *J. Chem. Soc., Chem. Commun.* **1979**, 1000.

(7) Levi, M.; Asad-Yellin, A.; Green, B. S.; Gedanken, G. A. *J. Chem. Soc., Chem. Commun.* **1980**, 847.
(8) Bertucci, C.; Lazzaroni, R.; Salvadori, P.; Johnson, W. C., Jr. *J. Chem. Soc., Chem. Commun.* **1981**, 590.
(9) Ledwith, A.; Chiellini, E.; Solaro, R. *Macromolecules* **1979**, *12*, 240.
(10) Chiellini, E. *Macromolecules* **1970**, *3*, 527.
(11) Luis, P. L.; Chiellini, E.; Franchini, P. F.; Orienti, M. *Makromol. Chem.* **1968**, *112*, 197.
(12) Delfini, M.; Conti, F.; Paci, M.; Segre, A. L.; Solaro, R.; Chiellini, E. *Macromolecules*, in press.
(13) Johnson, W. C., Jr. *Rev. Sci. Instrum.* **1971**, *42*, 1283.
(14) Robin, M. B. "Higher Excited States of Polyatomic Molecules"; Academic Press: New York, 1974; Vol. 1, p 265.
(15) Salvadori, P.; Bertucci, C., to be published.
(16) Ciardelli, F.; Chiellini, E.; Carlini, C.; Pieroni, O.; Salvadori, P.; Menicagli, R. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 62*, 143.
(17) Chen, A. K.; Woody, R. W. *J. Am. Chem. Soc.* **1971**, *93*, 29.

Synthesis of Poly(*p*-hydroxy-α-methylstyrene) by Cationic Polymerization and Chemical Modification

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ABSTRACT: High molecular weight, soluble poly(*p*-hydroxy-α-methylstyrene) has been synthesized for the first time by cationic polymerization of *p*-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene with boron trifluoride etherate as an initiator in liquid sulfur dioxide followed by thermolytic deprotection. Cationic polymerization of *p*-acetoxy-α-methylstyrene in dichloromethane followed by hydrazinolysis afforded the title compound, but the polymerization was accompanied by partial cleavage of the protecting group. Conventional cationic polymerization of *p*-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene in dichloromethane resulted in formation of low molecular weight polymer accompanied by partial cleavage of the protecting group. Ether monomers, such as *p*-methoxy- and *p*-(ethoxymethoxy)-α-methylstyrenes, readily underwent cationic polymerization, while the *p*-(2-methoxyethoxy)methyl derivative suffered from partial deprotection and cross-linking. Removal of the ether protecting group was, in all cases, accompanied by chain degradation and/or cross-linking. Chemical modification of poly(α-methylstyrene) and poly(*p*-bromo-α-methylstyrene) by lithiation followed by hydroxylation produced cross-linked materials.

Introduction

The preparation of linear polymers containing phenolic functional groups has attracted a great deal of attention recently due to the potential use of these materials as antioxidants, resist resins for microlithography, etc. While high molecular weight poly(*p*-hydroxystyrene) has been successfully prepared,[1,2] the synthesis of the corresponding poly(α-methylstyrene) analogue, namely, poly(*p*-hydroxy-α-methylstyrene) (poly[*p*-(1-methylethenyl)-phenol] (VIII)), has remained very elusive and only low molecular weight oligomers have been reported in the literature.[3,4] Thus, Kamagami and Hamashima[3] obtained short oligomers of degree of polymerization (DP) 4–5 by UV or γ-ray irradiation of the solid monomer, *p*-hydroxy-α-methylstyrene ((1-methylethenyl)phenol (I)), at room temperature. However, no polymerization of I whatsoever was observed in solution. The cationic polymerization of I produced mostly dimers and trimers, with a very small amount of oligomers of DP up to 17.[4] Similar results, characterized by the formation of only 1–3% yields of higher oligomers (DP up to 16), were obtained by Braun and Meier in the cationic polymerization of 2,6-di-*tert*-butyl-4-(1-methylethenyl)phenol.[5] Better results were obtained in the radical copolymerization of I with vinyl comonomers.[3,6,7] Thus, copolymerization with acrylonitrile produced a highly alternating copolymer with number-average molecular weight (M_n) ~50 000.[3]

The successful synthesis of high molecular weight VIII is difficult mainly due to the fact that α-methylstyrenes are reluctant to undergo radical homopolymerization and that the *p*-hydroxyl group reacts with cationic initiators and growing ends as a Lewis base and with anionic initiators and growing ends as a Brønsted acid. In consequence, our approach to the synthesis of VIII involves the polymerization of monomers with the hydroxyl group protected followed by removal of the protecting group to generate the free phenolic polymer. This paper reports the synthesis of VIII by cationic polymerization of several new protected monomers (IV) and subsequent chemical modification of the polymers (V) by deprotection. Attempts to prepare VIII directly by chemical modification of poly(α-methylstyrene) (VI) and its *p*-bromo derivative (VII) are also described.

Results and Discussion

Monomer Synthesis. A number of procedures have been reported for the preparation of I, including thermal[8] or base-catalyzed[9] cracking of 2,2-bis(*p*-hydroxyphenyl)-propane and catalytic dehydrogenation of *p*-(1-methylethyl)phenol,[10] but few polymerizations of the derivatives of I have been reported. Aliev and co-workers prepared the allyl and glycidyl ethers of I and succeeded in their copolymerization with styrene to yield cross-linked materials.[11]

A. Ester: *p*-Acetoxy-α-methylstyrene (IVa). Following the successful work of Arshady et al.[2] describing the preparation of poly(*p*-hydroxystyrene), our first approach to the synthesis of VIII was based on the synthesis of esters of I followed by polymerization and then hydrolysis to provide the free phenolic polymer (VIII). We

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