Formation of Phenolic Resins: Mechanism and Time Dependence of the Reaction of Phenol and Hexamethylenetetramine As Studied by Carbon-13 Nuclear Magnetic Resonance and Fourier Transform Infrared Spectroscopy

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ABSTRACT: ^{13}C NMR spectroscopy was used to study the reaction of phenol and hexamethylenetetramine at 100 °C as the reaction proceeded in the spectrometer probe. Analysis of sequential spectra revealed the presence of primary, secondary, and tertiary hydroxybenzylamines as reaction intermediates. The growth and decay of these intermediates as well as the formation of the bridging methylene carbon system were conveniently monitored. The crude time dependence of ^{13}C NMR signals enabled a qualitative evaluation of rate processes occurring in the complex reaction. Hexamethylenetetramine disappeared early in the reaction, and phenol displayed an early preference for reaction at the ortho position. Branching took place surprisingly late in the reaction. Fourier transform infrared spectroscopy was less informative and produced a different disappearance of hexamethylenetetramine.

Although phenolic resins have been used for many decades, detailed chemical understanding of their formation and cure has been speculative and not fully elucidated.[2-5] Significant progress in performance characteristics will not occur unless intimate knowledge concerning the structure, the mechanism, and the kinetics of resin formation and cure is obtained. A large number of analytical tools have already been utilized to gain such insight, including kinetic,[6] thermal,[7] and separation[8] methods. Of the spectroscopic techniques, NMR and IR have proven to be most illuminating. Detailed information about resin structure has been provided by ^{1}H[9-11] and especially ^{13}C NMR spectroscopy.[12-18] Infrared spectroscopy has elucidated degradation mechanisms of cured novalacs as well as structural features.[19-22]

The NMR and IR approaches have not been extensively used to obtain information during resin formation or cure. Kopf and Wagner successfully utilized ^{1}H NMR to study the reaction of phenols with curing agents and were thus able to identify reaction intermediates such as benzoxazines and benzylamines.[23] It was anticipated that ^{13}C NMR would provide additional and more revealing reaction details. For example, ^{13}C NMR was successfully used to study epoxy-curing mechanisms.[24]

We have used ^{13}C NMR and Fourier transform IR (FT IR) spectroscopy to study the mechanism and kinetics of phenolic resin formation. The reaction of phenol and hexamethylenetetramine (HEXA) was performed in situ so that ^{13}C NMR spectra could be obtained as a function of time. Analysis of these sequential spectra revealed the presence of primary, secondary, and tertiary hydroxybenzylamines as reactive intermediates.

In addition, the time dependence of HEXA disappearance, intermediate formation and destruction, and phenolic resin formation was obtained. The same reaction was studied by FT IR spectroscopy and spectral changes were noted.

Experimental Section

Sample Preparation. Phenol (ACS Reagent Grade) and HEXA (Aldrich) were ground to powders and screened to 80 mesh. The phenol/HEXA mixture used in all experiments was prepared by mixing overnight on a ball mill 100 g (1.1 mol) of phenol and 21 g (0.15 mol) of HEXA. Portions of this mixture were used for the in situ ^{13}C NMR experiments. Samples for FT IR measurements were obtained by reacting the phenol/HEXA mixture in an Erlenmeyer flask. The mixture was magnetically stirred while the flask was in a boiling water bath (98 °C). Aliquots were periodically withdrawn from the flask and quenched in ice water.

^{13}C NMR Measurements. Proton-decoupled ^{13}C NMR spectra were obtained on a Varian XL-100 NMR spectrometer equipped with a Nicolet TT-100 pulse unit. A 90° pulse took 14.9 μs and the time between pulses was 5 s. Time domain data were collected over 4K computer points and the sweep width was 5000 Hz. The spectrometer was equipped with a 4-pole Butterworth filter, and quadrature phase detection was used to detect NMR signals. An external ^{19}F NMR signal was used for field-frequency lock. Carbon-13 chemical shifts were measured relative to HEXA or the unsubstituted ortho carbon of phenol and converted to the Me_4Si scale with the relationships $\delta(Me_4Si) = \delta(HEXA) + 74.6$ and $\delta(Me_4Si) = \delta(ortho) + 117.7$.

The phenol/HEXA mixture was charged into a 10-mm-o.d. NMR tube, and the NMR tube cap was perforated to relieve pressure from evolving gases. The NMR tube was then placed in the spectrometer probe, which had been preequilibrated to 100 °C. Data acquisition commenced as soon as the tube was placed in the probe. Spectra were collected as a function of time. Each time domain spectrum consisted of 64 free-induction decays and took 5.04 min to collect. Fourier transformation was performed after the reaction was terminated.

FT IR Measurements. A Nicolet 7199 FT IR spectrometer was used for FT IR measurements. The spectral resolution was 2 cm^{-1} and 400 scans were recorded. Happ-Genzel apodization was applied before Fourier transformation. Interferograms were recorded over 8K computer points and 32K computer points were transformed. Spectra were run as Nujol mulls.

Results and Discussion

^{13}C NMR Spectroscopy. Table I contains assignments and a summation of all the carbon-13 chemical shifts observed during the reaction of phenol and HEXA.

Alkyl Carbons. Figure 1 shows the alkyl carbon region of the ten ^{13}C NMR spectra obtained while the reaction was proceeding in the spectrometer probe. The signal from HEXA only appeared in the first two reaction periods, indicating an early and rapid loss of this reactant. The alkyl region of the spectrum from reaction period 1 displayed only the HEXA carbon while the spectrum obtained from reaction period 2 showed that dramatic changes had occurred. The HEXA signal was substantially diminished and a number of upfield signals appeared. Three new signals occurring at 56.9, 51.1, and 44.9 ppm were assigned to tris(hydroxybenzyl)amines, bis(hydroxybenzyl)amines, and hydroxybenzylamines, respectively, by chemical shift comparison to literature values of the parent benzylamines.[25] Other low-intensity signals close to the above carbon-13 chemical shifts were detected and, presumably, are from analogues of the amines. Interest-

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Table I
Carbon-13 Chemical Shifts[a] and Assignments for the Reaction Products of Phenol and HEXA

chemical shift	assignments[b]
157.6	C-1 of phenol
155.9	C-1 of **2a,b**; C-5 of **2c-f**
153.6	C-1′ of **2a-d**; C-3′ of **2e,b**
151.8	C-1 of **3**
135.8, 134.6	C-2 of **1b**
132.6, 130.6	C-2, C-6′ of **2**; C-2′ of **2a,c,e**; C-4′ of **2b,d,f**
129.4, 127.8	C-2, C-3, C-4, C-5, C-6 of **3**; C-3, C-5 of **2a,b**; C-1, C-3 of **2c-f**; C-3′, C-5′ of **2a-d**; C-1′, C-5′ of **2e,f**
125.2, 124.7, 123.7	C-2 of **1a** (m = 2, 1)
122.8, 121.7	C-4 of phenol; C-4 of **2a,b**; C-4′ of **2a,c**
118.0, 117.7	C-2, C-6 of phenol; C-6 of **2a,b**; C-2′ of **2b,d**; C-2′ of **2b**; C-4′ of **2e**
74.6	carbons of HEXA
59.0, 53.3, 52.5	amine-type carbons
56.9	CH_2 of **1** (m = 3)
51.1	CH_2 of **1** (m = 2)
44.9	CH_2 of **1** (m = 1)
41.8	CH_2 of **2e,f**
36.8	CH_2 of **2c,d**
33.1, 32.6	CH_2 of **2a,b**

[a] In ppm from Me_4Si. [b] Assignments are made with reference to the structural representations shown in Scheme I.

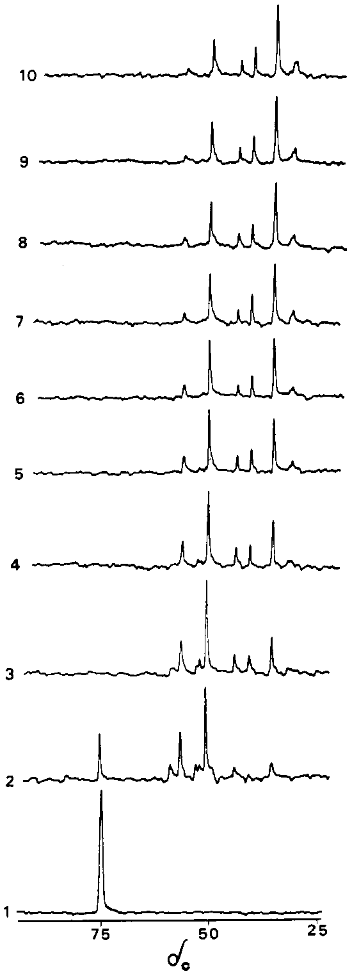


Figure 1. Sequential ^{13}C NMR spectra showing the alkyl carbon region.

ingly, the spectrum from reaction period 2 revealed that the signals from bis- and tris(hydroxybenzyl)amines were larger than that from hydroxybenzylamines.

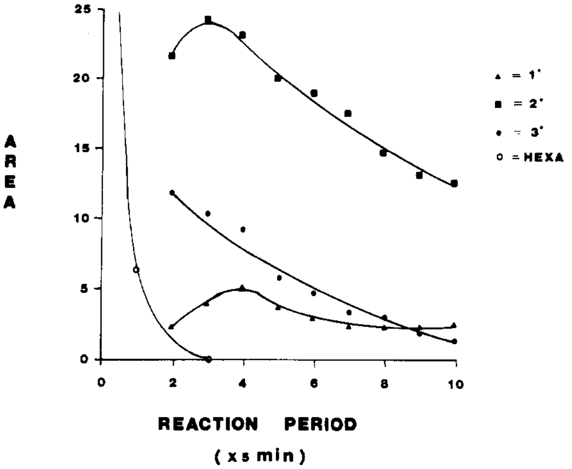


Figure 2. Apparent time dependence plots for HEXA and the intermediate primary, secondary, and tertiary hydroxybenzylamines.

An additional low-level signal detected in the alkyl region of the spectrum from reaction period 2 occurred at 36.6 ppm and was assigned to a 2,4′-methylene carbon bridging phenol rings.

Examination of Figure 1 shows that, with time, the signals from the hydroxybenzylamines increased and then decayed with the onset of phenolic resin formation. The hydroxybenzylamines are thus identified as reactive intermediates. Phenolic resin formation was indicated by the continued growth of bridging methylene carbons at 41.8, 36.8, and 33.1 ppm. The carbon-13 chemical shifts of the bridging methylene carbons are known to be separated according to their spatial relationship to hydroxyl.[18] Thus, the signal at 41.8 ppm was assigned to 4,4′-methylene carbons, the signal at 36.8 ppm to 2,4′-methylene carbons, and the signal at 33.1 ppm to 2,2′-methylene carbons.

The relative areas of the signals in Figure 1 were measured and plotted against the reaction period to give an apparent time-dependent profile of the identified species. The apparent time-dependent plot thus obtained is only an approximation to the actual time dependence as peak areas will be distorted by nuclear relaxation[26] and by the effects of signal accumulation.[27] Knowledge of the carbon-13 spin–lattice relaxation time (T_1) of pertinent carbon atoms under these reaction conditions would facilitate the extraction of rate constants. Nevertheless, the time evolution of the reaction can be crudely indicated.[28]

Figure 2 shows the apparent time dependence plot for HEXA and for the intermediate hydroxybenzylamines. This figure graphically illustrates the dramatic loss of HEXA in the early stages of the reaction. Bis(hydroxybenzyl)amines were the most abundant amines and their concentration maximized during reaction period 3 and then steadily decreased. Tris(hydroxybenzyl)amines apparently maximized very early in the reaction and then decreased. Hydroxybenzylamine production maximized approximately during reaction period 4 and then decreased to an apparent steady-state concentration.

Figure 3 shows the formation with time of the three different methylene carbons of the phenolic resin framework. Formation of the 2,2′- and the 4,4′-methylene carbons was fairly constant and approximately the same. However, the formation of the 2,4′-methylene linkage predominated and followed a different time dependence.

Aromatic Carbons. Figure 4 shows the phenoxy carbon region of the ten ^{13}C NMR spectra collected during the reaction. Phenol appeared at 157.6 ppm, mono-

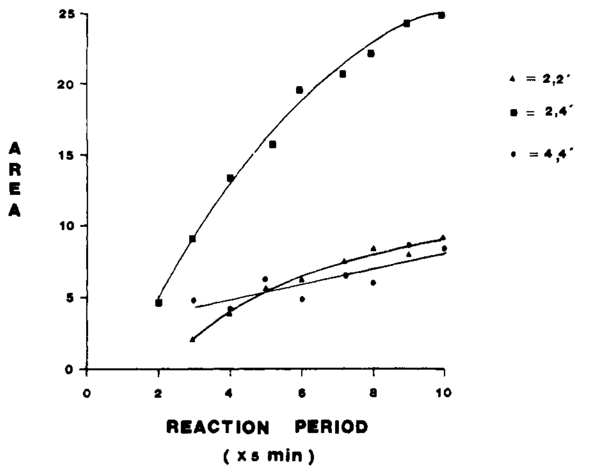


Figure 3. Apparent time dependence plots for bridging methylene carbons.

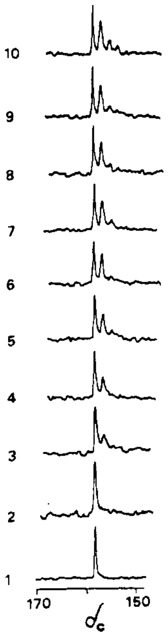


Figure 4. Sequential ^{1}C NMR spectra showing the phenoxy carbon region.

alkylated phenols at 155.9 ppm, dialkylated phenols at 153.6 ppm, and trialkylated phenols at 151.8 ppm. Thus, this region allowed for the approximate determination of when the species were formed. The apparent time dependences of these species are visualized in Figure 5. There is an apparent monotonic decrease in phenol which levels off at reaction periods 7–10. Onset of trialkylation was detected during reaction period 8. The detection of trialkylated phenols may be taken as a crude estimate of the point when branching of the resin commences. It is interesting to note how late branching occurred in this reaction. Furthermore, since the phenol concentration remains essentially constant in reaction periods 7–10, branching must take place predominantly by reactions between oligomers and hydroxybenzylamines.

Figure 6 displays the ortho, meta, and para aromatic carbon region of the ten ^{13}C NMR spectra generated during the reaction. Only the carbons of phenol were detected in the spectrum from reaction period 1. The spectra of reaction period 2 showed these signals developing fine structure as well as new peaks at 125.2, 124.7, and 123.7 ppm. The latter signals decreased with time and were assigned to the alkylated carbons of di- and tribenzylamines containing 2-hydroxy groups. The spectrum from reaction period 4 displayed the onset of new peaks at 135.8 and 134.6 ppm and were assigned to the alkylated carbons of mono-, di- and tribenzylamines containing 4-hydroxy groups.

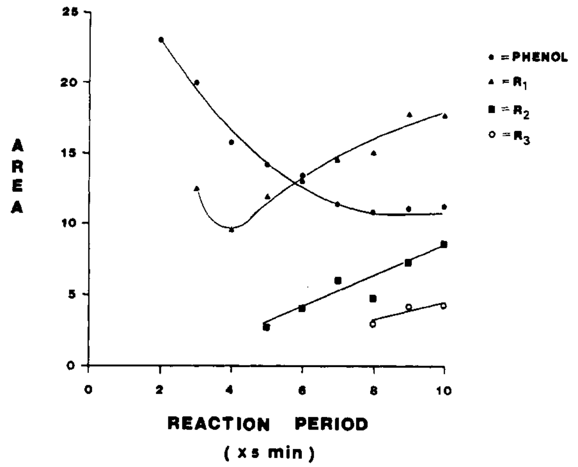


Figure 5. Apparent time dependence plots for the phenoxy carbons of phenol, monoalkylated phenols (R_1), dialkylated phenols (R_2), and trialkylated phenols (R_3).

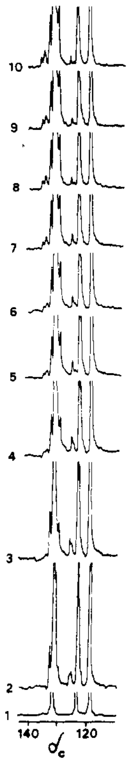


Figure 6. Sequential ^{13}C NMR spectra showing the ortho, meta, and para carbon region.

Thus, under these reaction conditions, there appeared to be a preference for formation of ortho-alkylated amines in the early stages of the reaction, with para-alkylated amines manifesting themselves in the later stages of the reaction.

The alkylation of ortho and para phenol carbons may be monitored by observing the changes in the areas of these unsubstituted carbons (C-2 and C-6 at 117.7–118.0 ppm and C-4 at 121.7–122.8 ppm). The unsubstituted ortho/para carbon ratio for the first seven reaction periods was less than 2, indicating preferential alkylation of ortho positions. The last three reaction periods displayed a

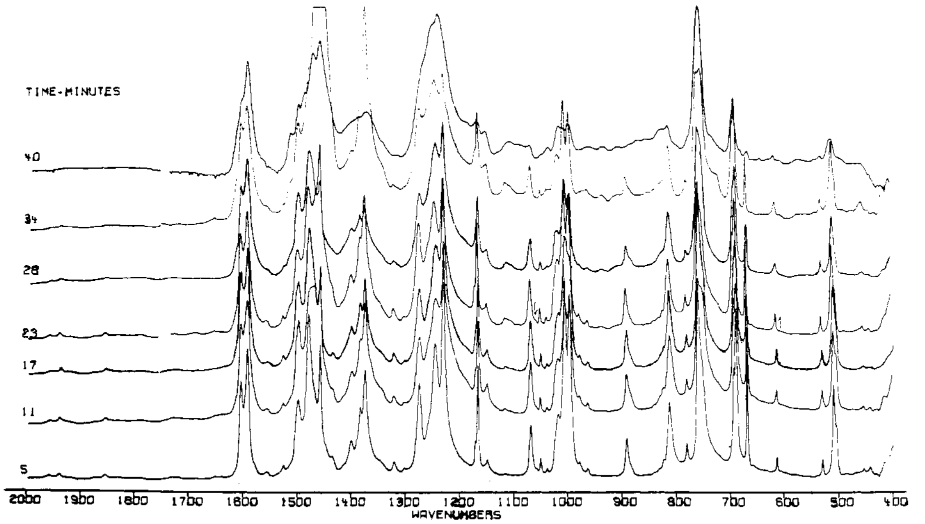


Figure 7. Sequential FT IR spectra in the 2000–400-cm^{-1} region.

dramatic increase of the ortho/para carbon ratio, indicating preferential reaction of para carbon. Interestingly, this increase coincides with the onset of branching, as indicated by the detection of phenoxy carbons from trialkylated phenol rings. This suggests that branching involves the substitution at para phenolic carbons.

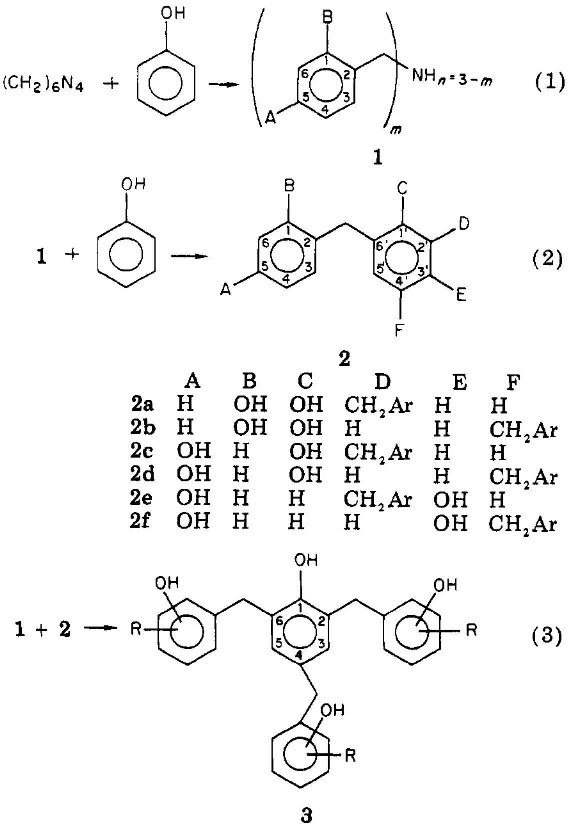
FT IR Spectroscopy. Figure 7 shows seven FT IR spectra between 2000–400 cm^{-1} of aliquots withdrawn from the reaction mixture at the indicated time intervals. The 4000–2000-cm^{-1} spectral region was typified by the large, broad hydroxyl stretching band and is not shown.

In general, the spectral lines became broader with time. The bands attributable to HEXA (1237, 1008, 673, 513 cm^{-1}) and those of phenol (1241, 1180, 1150, 1070, 882, 814, 691, 530 cm^{-1}) are seen to decrease with time. Unfortunately, bands attributable to reaction intermediates or products were not discernible, presumably because of interference from the IR bands of starting materials. Spectral subtraction proved difficult because of the general line-broadening phenomenon and because all signal intensities are changing.

Interestingly, the FT IR data revealed that HEXA was disappearing at a different rate than indicated by the ^{13}C NMR experiments. The two experimental approaches gave two different disappearance rates of HEXA, perhaps due, in part, to the great differences in detectability of the two techniques or to the way the two different experiments were physically performed.

Mechanism. The ^{13}C NMR results lead to the simplified reaction sequence given in Scheme I.

Scheme I



	A	B	C	D	E	F
2a	H	OH	OH	CH$_2$Ar	H	H
2b	H	OH	OH	H	H	CH$_2$Ar
2c	OH	H	OH	CH$_2$Ar	H	H
2d	OH	H	OH	H	H	CH$_2$Ar
2e	OH	H	H	CH$_2$Ar	OH	H
2f	OH	H	H	H	OH	CH$_2$Ar

3

There is a rapid reaction of phenol and HEXA, leading to the production of primary, secondary, and tertiary hydroxybenzylamines as reactive intermediates (eq 1). Evidence for a sequential breakdown of HEXA or for the production of benzoxazines[23] was not found under these reaction conditions, as signals from carbons bearing two nitrogen atoms or a nitrogen and an oxygen atom could not be detected. The rapid loss of HEXA was consistent with the early high concentrations of secondary and tertiary hydroxybenzylamines. The structure of the hydroxybenzylamines displayed an early preference for 2-hydroxybenzylamine (**1a**) formation with 4-hydroxybenzylamine (**1b**) formation manifesting itself during reaction period 4. The ratio of the unsubstituted ortho/para carbons also reflected this early preference for reaction at the ortho position. The signals from the intermediate hydroxybenzylamines decayed with appearance of the methylene bridges typical of the phenolic resin (eq 2). Secondary and tertiary benzylamines decayed at a faster rate than primary benzylamines. The production of 2,4-methylene carbon types dominated, which indicated that unsubstituted para carbons preferentially combine with methylene carbons of benzylamines which predominantly have 2-hydroxy groups. Finally, the onset of branching takes place late in the reaction and involves the hydroxybenzylamines (1) rather than free phenol (eq 3). The concentration of phenol remained constant during growth of trialkylated or branched phenolic species. Branching was also reflected in the dramatic increase of the unsubstituted ortho/para carbon ratio late in the reaction. This also implies that branching involves the alkylation of para phenolic carbons.

In conclusion, ^{13}C NMR and FT IR spectroscopy have provided insight into the very complex reaction of phenol and HEXA. ^{13}C NMR spectroscopy was especially informative. The identification and general structure of intermediate hydroxybenzylamines were found. The time dependence of HEXA disappearance, intermediate growth and decay, and the formation of bridging methylenes could be conveniently followed. Branching could also be detected and was found to occur late in the reaction. Additional work using diverse methylene sources as well as different starting conditions will prove to be equally rewarding.

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Conformation of Polymers with Mesogenic Groups and Flexible Spacers in the Main Chain in Dilute Solution and in the Isotropic Melt

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ABSTRACT: The magnetic birefringence of solutions (Cotton-Mouton effect) of various polyesters with mesogenic moieties and flexible spacers in the main chain as well as of some low molecular weight model compounds is described. There is no significant difference in the value of the Cotton-Mouton constant for polyesters in solution, low molecular weight model compounds in solution, and some polyesters in the isotropic melt. The conformation of this type of mesogenic polyester in isotropic solution and in the isotropic melt is consistent with a random coil conformation. The presence of chiral centers along the backbone has little influence on the rigidity of the polyester in the isotropic solution.

Polymers with mesogenic groups in the main chain represent an interesting class of macromolecules which can display in bulk nematic, cholesteric, and smectic mesophases.[1-4] We have recently synthesized a certain number of various polymers of this class and in this paper report the results of magnetic birefringence measurements performed on dilute solutions and isotropic melts of these polymers. Such studies are of interest because of the possibility of the formation of intramolecular order in such polymers. This possibility was discussed theoretically by Grossberg.[5]

Table I

polymer	[η], dL/g	$\bar{M}_n$
SEB-5	0.40	
SEB-7	0.23	4500
MAA*-8	0.38	
DDA-8	0.76	
50:50 MAA*/DDA-8	0.50	10800
MAA*-9	0.42	7850
50:50 MAA*/DDA-9	0.58	10815
DDA-9	1.02	20000

Experimental Section

Measurements of magnetically induced birefringence, Δn, were

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