

In conclusion,  $^{13}\text{C}$  NMR and FT IR spectroscopy have provided insight into the very complex reaction of phenol and HEXA.  $^{13}\text{C}$  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.<sup>1-4</sup> 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.<sup>5</sup>

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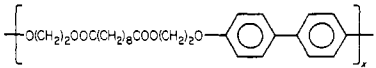
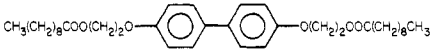
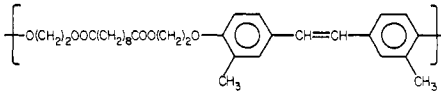
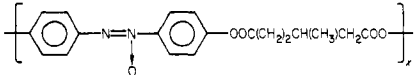
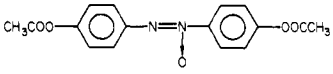
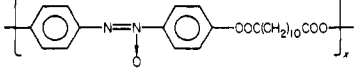
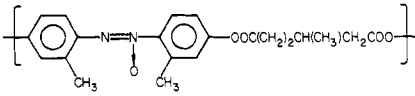
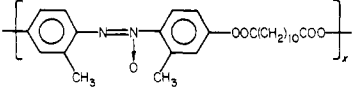
Table I

polymer	$[\eta]$ , 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,  $\Delta n$ , were

**Table II**  
**Specific Cotton-Mouton Constants of Various Polymers and Monomeric Models in Dilute Solution at Room Temperature and  $\lambda = 632.8$  nm**

sample	structure	solvent	$(CM)' \times 10^{-4} T^{-2}$ cm <sup>-1</sup> (w/w)
SEB-5		1:1 <i>m</i> -cresol/ Cl <sub>2</sub> CHCHCl <sub>2</sub>	1.25
model for SEB-5		Cl <sub>2</sub> CHCHCl <sub>2</sub>	0.73
SEB-7		CHCl <sub>3</sub>	1.31
MAA-8		Cl <sub>2</sub> CHCHCl <sub>2</sub>	1.6
model for MAA-8		Cl <sub>2</sub> CHCHCl <sub>2</sub>	1.75
DDA-8		Cl <sub>2</sub> CHCHCl <sub>2</sub>	1.5
50:50 MAA*/DDA-8	1:1 copolymer of MAA* (chiral) and DDA	Cl <sub>2</sub> CHCHCl <sub>2</sub>	1.58
MAA-9		Cl <sub>2</sub> CHCHCl <sub>2</sub>	1.16
MAA*-9	as above with MAA* (chiral)	Cl <sub>2</sub> CHCHCl <sub>2</sub>	1.20
DDA-9		Cl <sub>2</sub> CHCHCl <sub>2</sub>	0.93
50:50 MAA*/DDA-9	1:1 copolymer of MAA* chiral and DDA	Cl <sub>2</sub> CHCHCl <sub>2</sub>	0.87
SEB-7		isotropic melt ( <i>t</i> <sup>o</sup> = 135 °C)	1.35
benzene		liquid ( <i>t</i> <sup>o</sup> = 20 °C)	0.50

performed on 0–6% (w/w) solutions of polymers, on solutions of some low molecular weight model compounds, and on polymer melts (see Tables I and II), using a slightly modified<sup>6</sup> version of a technique described earlier.<sup>7</sup> At the sample length used (3 cm) and a wavelength  $\lambda$  of 632.8 nm the resolution in  $\Delta n$  was about  $10^{-10}$ . Up to the maximum of the applied magnetic field ( $H$ ), 13.5 T, all samples showed a strictly linear increase of  $\Delta n$  with  $H^2$ ; hence a classical Cotton-Mouton effect was evident. The experimental Cotton-Mouton constants, CM, were calculated from  $\Delta n = (CM)\lambda H^2$ . The specific Cotton-Mouton constants,  $(CM)'$ , of polymers and model compounds were deduced from CM as follows: The Cotton-Mouton constant of a binary mixture (such as our solvent-solute system) is given<sup>8</sup> to a good approximation by

$$\frac{\bar{n}}{(\bar{n}^2 + 2)^2} (CM) = \frac{n_s}{(n_s^2 + 2)^2} \left( \frac{c}{1+c} \right) (CM)' + \frac{n_0}{(n_0^2 + 2)^2} \left( 1 - \frac{c}{1+c} \right) (CM)_0 \quad (1)$$

where  $\bar{n}$ ,  $n_s$ , and  $n_0$  are the refractive indices of the mixture, the bulk sample (solute), and the solvent, respectively.  $c$  is the concentration of the sample expressed as weight of sample per weight of added solvent.  $c/(1+c)$  and  $1-c/(1+c)$  are the fractions of sample and solvent, respectively. For a dilute solution ( $c \ll 1$ ) and if  $n_s \sim n_0$ , eq 1 simplifies:

$$[CM - (CM)_0]/c = (CM)' \quad (2)$$

For a melt of the sample ( $c = \infty$ ), eq 1 yields

$$CM = (CM)' \quad (3)$$

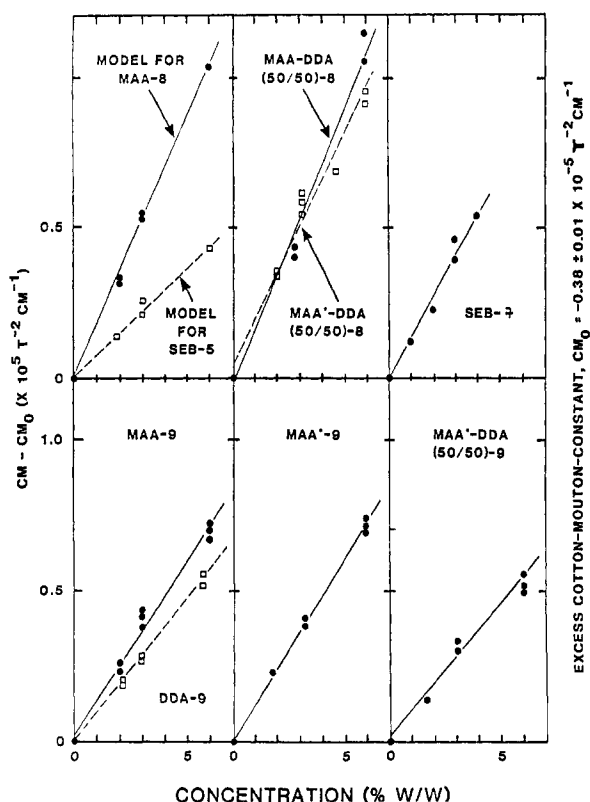
In this work the simplified equations (2) and (3) were used. This appears to be justified: In the case of SEB-7 in chloroform, for

example, the error introduced by ignoring the difference between  $n_0$  and  $n_s$  is of the order of 15%, which does not affect in any way our qualitative conclusions.

The polymers were all polyesters resulting from condensation of corresponding diols or diphenols with aliphatic diacids. Their synthesis and properties are described elsewhere.<sup>2,3,9,10</sup> The limiting viscosity numbers of SEB-5 and SEB-7 (see Table II for structures) were measured at 32 °C in a 1:1 (w/w) mixture of trichloroethane and *m*-cresol. For MAA-8 DDA-8, and the corresponding 50/50 copolymers of MAA-8 and DDA-8 (Table II), a 1:1 mixture of chloroform and *m*-cresol was used at 30 °C. The same solvent mixture was used for the MAA-9 and DDA-9 polyesters (Table II), differing from the MAA-8 and DDA-8 by the presence of methyl groups in the ortho position with respect to the azoxy linkage. The number-average molecular weights,  $\bar{M}_n$ , were determined by vapor pressure osmometry (VPO) in chloroform at 30 °C with a Knauer vapor pressure osmometer. SEB-5, MAA\*-8 and DDA-8 were not soluble enough to give reliable  $\bar{M}_n$  values from VPO.

## Results and Discussion

Table I gives typical characteristics of the polymers used. As demonstrated by a few examples in Figure 1, all samples showed a linear increase of CM with concentration, in agreement with eq 2, indicating the absence of intermolecular association and orientational correlations up to at least 6% (w/w). The absence of large aggregates is also confirmed by the strict linearity of  $\Delta n$  vs.  $H^2$  combined with the low values of  $[\eta]$ . Least-squares-fitted slopes of these plots therefore yield the specific  $(CM)'$  values of the polymers and model compounds which are reported in Table II.



**Figure 1.** Concentration dependence of the Cotton-Mouton constants of various polyesters (see Table II). Solvent  $CM$  values have been subtracted [ $(CM)_0 = -(0.38 \pm 0.01) \times 10^{-5} T^{-2} \text{ cm}^{-1}$  for  $\text{CHCl}_2\text{CHCl}_2$ ,  $-0.66 \times 10^{-5} T^{-2} \text{ cm}^{-1}$  for  $\text{CHCl}_3$ , and  $+2.52 \times 10^{-5} T^{-2}$  for 1:1 *m*-cresol/ $\text{CHCl}_2\text{CHCl}_2$ ]. Continuous and dashed lines refer to (●) and (□), respectively, and are least-squares fits through the data points. Their slopes are given in Table II.

One can remark immediately that the  $(CM)'$  values for the mesogenic polyesters in dilute solution are close to the values of the (monomeric) model compounds and of other simple aromatic molecules, for example, benzene, and flexible polymers, for example, polystyrene [ $(CM)' = 1.27 \times 10^{-4} T^{-2} \text{ cm}^{-1}$  in tetrachloroethylene<sup>6</sup>] or polycarbonate [ $(CM)' = 0.96 \times 10^{-4}$  in chloroform<sup>11,12</sup>]; they are, however, 1–2 orders of magnitude smaller than  $(CM)'$  values of typical semirigid (wormlike) polymers, such as polybenzamide<sup>13</sup> or DNA.<sup>14</sup> Therefore, at certain temperatures these polyesters, although liquid crystalline in the melt, appear to be very flexible coils in dilute solution.

The conformation of an ideal Gaussian chain is described in terms of the persistence length  $P$  and the contour length  $\Lambda$ . The rigidity of the chain is given by  $P$ . For a wormlike chain, with  $\Lambda$  much larger than  $P$ ,  $(CM)'$  is simply related to  $P$  by  $(CM)' / (CM)_m' = 2P / 3l_0$ ,<sup>15</sup> where  $l_0$  is the length of a monomer unit (which is assumed to be rigid; i.e.,  $l_0 \ll P$ ) and  $(CM)_m'$  is its Cotton-Mouton constant. This model clearly fails for copolymers with rigid moieties connected by flexible spacers because the monomer unit cannot be considered stiff. Other more specific models—such as the isomeric state model—taking into account bond angle restrictions have been applied only to simpler polymers, for example, alkanes and polystyrene.<sup>16</sup> Thus we are left with the qualitative conclusion that the investigated polyesters are all characterized by persistence lengths (or Kuhn segment lengths) close to the length of the monomer unit.

Some significant features of our data for solutions are, however, noteworthy: chirality does not influence significantly the rigidity (MAA-9 vs. MAA\*-9, 50:50 MAA/DDA-8 vs. 50:50 MAA\*/DDA-9); the  $(CM)'$  values of the 8-containing polymers clearly exceed those of the 5-, 7-, and 9-containing samples. These differences can possibly be related to varying (even competing) contributions of the constituent molecular groups to the anisotropy of the diamagnetic susceptibility and of the optical polarizability. For example, it can be expected from bond anisotropies<sup>17</sup> that the SEB, DDA, and MAA groups tend to orient perpendicularly to the magnetic field  $H$ , whereas the 5-, 7-, 8-, and 9-containing aromatics orient parallel to  $H$ . The latter groups are dominant in all cases.

It is also noteworthy that SEB-7 has very similar  $(CM)'$  values in the isotropic melt and in dilute solution, indicating a coiled conformation of this polymer even in the melt (at temperatures well above the nematic-to-isotropic transition).

In conclusion, magnetic birefringence measurements performed on solutions of various polyesters with mesogenic groups and flexible spacers in the main chain and on low molecular weight model compounds are consistent with a random coil conformation and a high flexibility of these polymers. Because of the chemical complexity of the monomeric units, a quantitative interpretation of our data in terms of a parameter describing the chain rigidity is lacking. Nevertheless, the data show conclusively that the persistence length of these polymers in their dissolved and molten state does not substantially exceed the length of the monomeric unit.

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