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.

Acknowledgment. We are indebted to W. T. Schwartz, B. F. Dannels, and J. J. Duffy of the Durez Division, Hooker Chemicals and Plastics Corp., for helpful discussions.

References and Notes

(26) Under our pulse conditions, distortion of peak areas will be minimal (<10%) if the carbon-13 spin-lattice relaxation times are 2 s or less. A procedure for measuring carbon-13 spin-lattice relaxation times in an oligomerizing system of increasing viscosity is not obvious at this time. We would anticipate values of 2 s or less in this system because of molecular sizes and high viscosities.

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

A. Blumstein,* G. Maret,† and S. Vilasagar

Department of Chemistry, Polymer Program, University of Lowell, Lowell, Massachusetts 01854, and Hochfeld-Magnet Labor, Max-Planck-Institut für Festkörperforschung, P-38042 Grenoble-Cedex, France. Received December 15, 1980

ABSTRACT: The magnetic birefringence of solutions (Cotton–Mouton effect) of various polymers 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 polymers in solution, low molecular weight model compounds in solution, and some polymers 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 polymer 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 amatic 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

<table>
<thead>
<tr>
<th>polymer</th>
<th>$[\eta]$</th>
<th>dL/g</th>
<th>$M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEB-5</td>
<td>0.40</td>
<td></td>
<td>4500</td>
</tr>
<tr>
<td>SEB-7</td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MAA*-8</td>
<td>0.38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DDA-8</td>
<td>0.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50:50 MAA*/DDA-8</td>
<td>0.50</td>
<td>10800</td>
<td></td>
</tr>
<tr>
<td>MAA*-9</td>
<td>0.42</td>
<td></td>
<td>7850</td>
</tr>
<tr>
<td>50:50 MAA*/DDA-9</td>
<td>0.56</td>
<td>10515</td>
<td></td>
</tr>
<tr>
<td>DDA-9</td>
<td>1.02</td>
<td></td>
<td>20000</td>
</tr>
</tbody>
</table>

Experimental Section

Measurements of magnetically induced birefringence, $\Delta n$, were...
Table I

Specific Cotton–Mouton Constants of Various Polymers and Monomeric Models in Dilute Solution at Room Temperature and \( \lambda = 632.8 \) nm

<table>
<thead>
<tr>
<th>sample</th>
<th>structure</th>
<th>solvent</th>
<th>((CM) \times 10^{-4} T^{-1}) cm(^{-1}) (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEB-5</td>
<td><img src="image" alt="structure" /></td>
<td>1:1 m-cresol/Cl(_2)CHCHCl(_2)</td>
<td>1.25</td>
</tr>
<tr>
<td>model for SEB-5</td>
<td><img src="image" alt="structure" /></td>
<td>Cl(_2)CHCHCl(_2)</td>
<td>0.73</td>
</tr>
<tr>
<td>SEB-7</td>
<td><img src="image" alt="structure" /></td>
<td>CH(_3)Cl</td>
<td>1.31</td>
</tr>
<tr>
<td>MAA-8</td>
<td><img src="image" alt="structure" /></td>
<td>Cl(_2)CHCHCl(_2)</td>
<td>1.6</td>
</tr>
<tr>
<td>model for MAA-8</td>
<td><img src="image" alt="structure" /></td>
<td>Cl(_2)CHCHCl(_2)</td>
<td>1.75</td>
</tr>
<tr>
<td>DDA-8</td>
<td><img src="image" alt="structure" /></td>
<td>Cl(_2)CHCHCl(_2)</td>
<td>1.5</td>
</tr>
<tr>
<td>50:50 MAA*/DDA-8</td>
<td>1:1 copolymer of MAA* (chiral) and DDA</td>
<td>Cl(_2)CHCHCl(_2)</td>
<td>1.58</td>
</tr>
<tr>
<td>MAA*-9</td>
<td>as above with MAA* (chiral)</td>
<td>Cl(_2)CHCHCl(_2)</td>
<td>1.20</td>
</tr>
<tr>
<td>DDA-9</td>
<td><img src="image" alt="structure" /></td>
<td>Cl(_2)CHCHCl(_2)</td>
<td>0.93</td>
</tr>
<tr>
<td>50:50 MAA*/DDA-9</td>
<td>1:1 copolymer of MAA* chiral and DDA</td>
<td>Cl(_2)CHCHCl(_2)</td>
<td>0.87</td>
</tr>
<tr>
<td>SEB-7</td>
<td>benzene</td>
<td>1.35</td>
<td></td>
</tr>
</tbody>
</table>

**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.
of various polyesters (see Table II). Continuous and dashed lines refer to (CM)" and (CM)', 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 x 10^{-4} T^{-2} cm^{2} for CHCl_{3}, 0.96 x 10^{-4} T^{-2} cm^{2} for CHCl_{3}, and +2.52 x 10^{-4} T^{-2} for 1:1 m-cresol/CHCl_{3}]. Continuous and dashed lines refer to (O) and (2), respectively, and are least-squares fits through the data points. Their slopes are given in Table II.

The conformation of an ideal Gaussian chain is described in terms of the persistence length P and the contour length L. The rigidity of the chain is given by P. For a wormlike chain, with a much larger than P, (CM)' is simply related to P by (CM)' = 2P/3L_{0}, where L_{0} is the length of a monomer unit (which is assumed to be rigid; i.e., L_{0} << P) and (CM)' 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, alkane and polystyrene. 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 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.

Acknowledgment. A.B. and S.V. acknowledge support of the National Science Foundation (Polymers Program, Grant DMR-7925059).

References and Notes