Polymerization under magnetic field (Part 7)—Synthesis and characterization of a liquid crystal polymer

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A lyotropic liquid crystal (LC) poly(amide hydrazide) was synthesized from a diamine, \(N,N'\)-bis(4-aminobenzoyl) hydrazine (BABH) and terephthaloyl chloride (TC) in presence and absence of magnetic field (MF) of 4 kg. The polymer prepared with and without MF was characterized by viscosity and density measurements, IR spectroscopy, X-ray diffractometry, and TGA and DSC analysis. The polymer prepared under MF was of higher inherent viscosity. The molecular weight (MW) of the polymer determined by IR spectroscopy was also higher when prepared under MF. The polymer prepared under MF was more thermostable than that obtained without MF.

Although in early eighties a few polymerizations and crosslinking reactions were studied under magnetic field (MF), recently greater attention has been paid to study the structures and properties of polymers prepared under MF. The effect of MF on all aspects of polymerizations and polymers have been well documented in a recent review1.

The orientation of the LC polymer and to stabilize the alignment by freezing, crystallizing, drying or by gel formation by the application of magnetic field (MF) have been reported earlier23. The orientation of LC polymer by the application of MF and then freezing the oriented structure by crosslinking have also been studied44. Various LC vinyl monomers have been polymerized/copolymerized under MF to obtain highly oriented and crystalline polymers7-11. Polymerization of LC vinyl monomer, \(p-(4\)-ethoxyphenyliminomethylidyne\(-p\)-ethoxyaniline) in its nematic phase under a strong MF of 70 kg gave a LC polymer of the smectic A type11. The polymerization and copolymerization of monomers, di\((N-p\)-acryloyloxybenzylidene\)-\(p\)-diaminobenzene and \(N-(p\)-acryloyloxybenzylidene\)-\(p\)-n-butylaniline in their nematic phase gave smectic polymers having side chains aligned with the field and the polymer backbone chains confined to perpendicular to the side groups11. But the polymerization of both the monomers, di\((N-p\)-acryloyloxybenzylidene\)hydrazine and \(p\)-phenylene \(bis(N\)-methylene-\(p\)-aminostyrene) in their nematic state resulted in polymers with nematic order11. In these cases, by the application of MF, the LC monomers in their mesomorphic state are oriented and simultaneously polymerized by a free radical mechanism. The main objective of such polymerizations under MF is to obtain highly oriented polymers.

However, the polymerization of \(\gamma\)-benzyl-L-glutamate \(N\)-carboxy anhydride (BLG-NCA) to obtain a LC polymer, poly\((\gamma\)-benzyl-L-glutamate\) (PBLG), under MF (3.6 kg) provides an example where the monomer is not a vinyl monomer12. In this investigation a lyotropic LC polymer, poly(amide hydrazide) has been synthesized from a diamine, \(N,N'\)-bis(4-aminobenzoyl) hydrazine and terephthaloyl chloride by low temperature polycondensation method under MF. The polymer has been characterized to observe the MF effect.

Experimental Procedure

Materials

4-Nitrobenzoic acid (LOBA Chemie) was recrystallized from ethanol-water; m.p. 240-242°C (literature 241-242°C). Terephthalic acid
Results and Discussion

Synthesis of liquid crystal polymer—The reaction scheme for condensation polymerization of a diamine, BABH and a diacid chloride, TC, to obtain LC polymer, poly(amide hydrazide) may be presented below:

Characterization of the polymer

Viscosity measurement—The homogeneous reaction mixture, after 1 h of reaction, was directly used to prepare a 0.5% (w/v) polymer solution with proper dilution by DMAc/2.5% (w/v) LiCl used as polymerization medium, for determination of inherent viscosity. The inherent viscosity ($\eta_{inh}$) of the polymer solution was determined by a Ubbelohde suspended level viscometer at 30°C.

Density measurement—The densities of the powdered polymer samples were measured in dry benzene at 30°C using a pycnometer.

IR spectroscopy—IR spectra of the same amount of polymers prepared with and without MF were recorded with a Perkin Elmer 883 infrared spectrophotometer with KBr pellets.

X-ray diffractometry—Wide angle X-ray diffractographs for the powdered polymer samples were recorded with a Phillips PW 1840 X-ray diffractometer using Ni-filtered Cu Kα ($\lambda = 1.5418$ Å) radiation at a scanning speed of 3°/min.

Thermal analyses—Thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) of the powdered polymer samples were carried out with a Stanton Redcroft STA-625 thermal analyzer at a heating rate of 10°C/min in a nitrogen atmosphere.

Results and Discussion

Synthesis of liquid crystal polymer—The reaction scheme for condensation polymerization of a diamine, BABH and a diacid chloride, TC, to obtain LC polymer, poly(amide hydrazide) may be presented below:

Polymer yield and inherent viscosity—The polymer yield and the inherent viscosity of 0.5%
polymer solution prepared in presence and absence of MF are shown in Table 1. The influence of MF on the polymer yield is not observed. However, the inherent viscosity of the polymer increases when prepared under MF. The effect of MF on the inherent viscosity \( (\phi_{inh}) \) is calculated using the following equation:

\[
\phi_{inh} = \left( \frac{\eta_{inh}(H) - \eta_{inh}(O)}{\eta_{inh}(O)} \right) \times 100\%
\]

where, \( \eta_{inh}(H) \) and \( \eta_{inh}(O) \) are inherent viscosities of polymers prepared with and without MF respectively.

The inherent viscosity increases by 19.3\% by the application of MF of 4 kg (Table 1). This may be due to the orientation of the monomers at low temperature by the MF. Therefore, the chances of the monomers to react is enhanced. As a result, degree of polymerization and/or inherent viscosity increases. It should be mentioned here that the MF effect on the ring opening polymerization of \( \gamma \)-benzyl-L-glutamate \( N \)-carboxy anhydride (BLG-NCA) to obtain LC poly(\( \gamma \)-benzyl-L-glutamate) is reported in the literature \(^{12}\). The rate of acceleration is due to the suitable alignment of BLG-NCA monomers and/or growing polymer chains under the MF. The MW of the polymer obtained under MF (3.6 kg) was higher than that obtained without MF \(^{12}\).

**Table 1—Synthesis of LC Poly(amide hydrazide) in presence and absence of MF**

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>MF (kg)</th>
<th>Yield*</th>
<th>( \eta_{inh} )</th>
<th>( \phi_{inh} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM(_1)</td>
<td>0</td>
<td>83</td>
<td>1.50</td>
<td>19.3</td>
</tr>
<tr>
<td>BM(_2)</td>
<td>4</td>
<td>82</td>
<td>1.79</td>
<td></td>
</tr>
</tbody>
</table>

a. The values are the average of two measurements

**Density**—In general, the density of the fiber polymer was found to be dependent upon the structure, the degree of regularity of the structural units, and the degree of orientation and crystallinity. The aromatic poly(amide hydrazide)s possess higher densities. The very high densities are observed for all para-oriented poly(amide hydrazide)s due to the close packing of the aromatic rings which probably tend to lie in the plane parallel to the fiber axis. The densities of this poly(amide hydrazide) samples prepared with and without MF are 1.41 g/cm\(^3\) and 1.40 g/cm\(^3\) respectively. The reported value \(^{15}\) is 1.40 g/cm\(^3\). Thus MF has no influence on the density of this linear poly(amide hydrazide). Moreover, the effect of MF on the close packing in the crystal lattice is not also apparent from the X-ray diffraction study.

**IR analysis**—The polymers prepared with and without MF were analyzed by IR spectroscopy. Some important characteristic peaks are presented in Table 2. There is no distinguishable difference between the two IR spectra of the polymer prepared with and without MF. Therefore, the polymerization mechanism particularly the mode of monomer addition is not influenced under MF.

However, the degree of polymerization of the poly(amide hydrazide) prepared under MF is found to be higher as evident from the higher absorption intensity of the CONH linkage shown in Fig.1. The stretching vibration of C=O of COCl\(_2\) endgroup appears at 1800 cm\(^{-1}\) whereas stretching vibration of C=O of CONH appears at 1650 cm\(^{-1}\). The poly(amide hydrazide) was synthesized with equimolar diamine and diacid chloride. Therefore, considering one COCl\(_2\) end group in each polymer

**Table 2—Important characteristic IR peaks (\( \nu, \text{cm}^{-1} \)) of poly(amide hydrazide) prepared under MF**

<table>
<thead>
<tr>
<th>Polymer specification</th>
<th>CONH group</th>
<th>CONH–NCO</th>
<th>Aromatic ring C=C str.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM(_1)</td>
<td>1656 (s)</td>
<td>3266 (m)</td>
<td>1517 (s)</td>
</tr>
<tr>
<td>BM(_2)</td>
<td>1650 (s)</td>
<td>3265 (m)</td>
<td>1519 (s)</td>
</tr>
</tbody>
</table>

str. and def. mean stretching and deformation vibrations, respectively. s and m indicate strong and medium intensities of the peaks, respectively.
molecule and from the ratio of the absorption peak intensity of C=O of CONH to that of COCl, the molecular weight (MW) of the polymer has been calculated and presented in Table 3. The MW of the polymer prepared under MF is higher than that of the polymer prepared without MF.

X-ray Diffractometry—The polymers prepared with and without MF were analyzed by X-ray diffractometry. No difference is observed in the X-ray diffractographs of the polymers prepared with and without MF. This may be due to the linear addition of two monomers having functional group in the para positions during polymerization and no side chain to be oriented. All the polymers are poorly crystalline in nature. This poly(amide hydrazide) has also been reported to be poorly crystalline in nature\(^1\). Due to the presence of all \textit{para}-oriented aromatic rings linked by stiff polar amide and hydrazide groups, the rigid polymer chains should be close packed. As a result, they should be highly crystalline in nature. Precipitated samples of rigid aromatic polyamides, viz., poly(p-benzamide) and poly(p-phenylene terephthal-amide), have not been observed to be especially crystalline from X-ray diffractographs\(^1\), though their fibers have been known to be highly crystalline. However, Thanuja \textit{et al.}\(^1\) reported that the X-ray diffractographs of poly(amide hydrazide) containing azo groups in the main chain showed crystalline peaks. The discrepancy of our results from the literature may be explained in two ways: (i) the processing history may affect the crystallinity of the polymer and (ii) the larger particle size of the polymer powder, which cannot be finely powdered by grinding because of its plastic nature came in the way of better X-ray diffraction.

Thermal behaviour—The thermal decomposition characteristics of the polymer prepared with and without application of MF are shown by the TGA (Fig.2). The detailed decomposition behaviour in nitrogen atmosphere is presented in Table 4. The polymers undergo major weight losses in three steps. The initial weight loss of about 4% occurs between 80°C and 115°C possible due to loss of absorbed moisture. Between 345°C and 465°C, the polymers undergo a weight loss of about 7-9% due to loss of water liberated during cyclodehydration of the hydrazide groups to form 1,3,4-oxadiazole rings\(^1\).\(^1\)\(^8\)\(^9\)\(^10\). The third step weight losses are

<table>
<thead>
<tr>
<th>Polymer specification</th>
<th>MF (kg)</th>
<th>(\frac{l_{c=0}}{l_{c=0}}) of CONH</th>
<th>MW(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM(_1)</td>
<td>0</td>
<td>3.67</td>
<td>1600</td>
</tr>
<tr>
<td>BM(_2)</td>
<td>4</td>
<td>6.69</td>
<td>2800</td>
</tr>
</tbody>
</table>

\(^b\) based on the absorption peak intensity
\(^b\)Molecular weight of mer unit is 400

Fig. 1—IR spectra of poly(amide hydrazide) prepared in (a) presence and (b) absence of magnetic field (4 kg)

Fig. 2—TGA curves (heating rate = 10°C/min in nitrogen) of poly(amide hydrazide) prepared (a) with and (b) without magnetic field (4 kg)
Table 4—Thermal behaviour of poly(amide hydrazide) prepared under MF

<table>
<thead>
<tr>
<th>MF (kg)</th>
<th>Cyclo dehydration</th>
<th>Degradation</th>
<th>Residue (wt%) at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Starts at °C</td>
<td>Ends at °C</td>
<td>600 °C</td>
</tr>
<tr>
<td>0</td>
<td>345</td>
<td>465</td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>347</td>
<td>470</td>
<td>51</td>
</tr>
</tbody>
</table>

Fig. 3—DSC curves (heating rate = 10°C/min in nitrogen) of poly(amide hydrazide) prepared (a) with and (b) without magnetic field (4 kg)

associated with the degradation of the polymer. However, the thermal degradation is less for the polymer prepared under MF. This may be due to the higher molecular weight and other structural differences of the polymer prepared under MF.

DSC study was carried out in nitrogen atmosphere from room temperature to 560°C. The DSC curves for the polymers prepared with and without application of MF are shown in Fig. 3. However, major difference between these two curves is not observed. The endotherms centered around 85-105°C are due to loss of absorbed moisture and around 350-360°C due to cyclodehydration. The endotherms centered around 520-530°C appear to be the degradation of polymers.

Conclusion
The influence of MF on the polymer yield was not observed. However, the inherent viscosity and molecular weight (MW) of the polymer were increased by the application of MF (4 kg). This may be due to orientation of monomers at low temperature under MF which enhances the monomer addition resulting a polymer of higher MW. No MF effect is observed by density measurement and XRD analysis of the polymers. However, the thermal stability of the polymer prepared under MF is higher than that of the sample prepared without MF. This is because of the higher MW of the polymer prepared under MF.

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