Side-Chain Liquid Crystalline Ionomers. 1. Preparation through
Alkaline Hydrolysis and Characterization

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ABSTRACT: Side-chain liquid crystalline ionomers were obtained through alkaline hydrolysis of liquid crystal
line polyacrylates. In the case of a polyacrylate bearing a phenyl benzoate moiety in the mesogenic
group, partial hydrolysis using sodium hydroxide was found to be highly selective and give the sodium salt
of benzoic acid; as for a polycarbonate containing a biphenyl moiety in the side group, a hydrolysis reaction
resulted in the sodium salt of acrylic acid. Increasing the content of ionic groups led to a systematic depression
of the nematic to isotropic transition temperature. On the other hand, ionic aggregation had little effect on
the nematic to isotropic transition enthalpies as well as the glass transition temperatures of these new
materials, in particular for ionomers based on the polycarbonate containing a biphenyl moiety in the side group.

Introduction

Research and development of side-chain liquid crystal-
line polymers (LCPs) and ion-containing polymers, namely,
ionomers, are two distinct areas of polymer science.
Nevertheless, an ion-containing polymer displaying liquid
crystalline phases is obviously of great interest for both
basic and applied studies. For instance, such a more
complicated system could combine the characteristic features of both LCPs and ionomers, leading to new and
useful materials. One the other hand, one would like to
know the fundamental link between ionic aggregation found in ionomers and the behavior of liquid crystalline
phases in terms of molecular order and stability.

Very few investigations on the synthesis of side-chain
liquid crystalline ionomers have so far been reported. Zentel
et al.1 prepared copolymers made from mesogenic and ferrocene-containing monomers and obtained ionomers
by oxidation of the ferrocene groups. The method employed by Gramain et al.2 was based on simultaneous
quaternization and polymerization of 4-vinylpyridine in
the presence of a mesogenic group, which resulted in a
LCF containing ionic charge. As for Blumstein and co-
workers,3 they prepared LCPs with side groups containing
a pyridine-type unit which was quaternized to form
ionomers. More recently, in this laboratory we have shown4
that partial neutralization of a copolymer obtained from
a mesogenic methacrylate monomer and methacrylic acid
comonomer resulted in ionomers exhibiting liquid crystal-
line phases.

In the present study, we prepared side-chain liquid
crystalline ionomers through direct alkaline hydrolysis.
To demonstrate the utility of this method, two polycacy-
lates bearing representative mesogenic side groups, namely,
phenyl benzoate and biphenyl moieties, were used. Alkaline hydrolysis is a known method for obtaining
conventional acrylate or methacrylate ionomers;6 the main
interest of exploring this technique for liquid crystalline
ionomers is 2-fold. First, a new and convenient way of
making side-chain liquid crystalline ionomers can be
established. Second, the liquid crystalline ionomers can
be used to investigate the influence of the intrinsically
oriented microstructure on the macroscopic orientation
process under different aligning fields, since random
incorporation of a small amount of ionic groups could
readily induce a perturbation in the oriented microstruc-

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Experimental Section

Polymer Preparation. The two liquid crystalline poly-
crulates used for alkaline hydrolysis were prepared by methods
described in the literature.6,7 They have the following structures:

Estimated by GPC using polystyrene standards, the sample
containing the phenyl benzoate moiety in the side group, denoted
as PBA, has a number-average molecular weight of ca. 47 000
(Mn/Mw = 1.54), and the sample with the biphenyl moiety in the
side group, referred to as BiPBA, has a Mn of ca. 79 000 (Mn/Mw
= 1.78). Both polymers exhibit a nematic liquid crystalline phase,
which is consistent with the literature.6,7

Alkaline Hydrolysis. The following procedures was used to
partially hydrolyze both PBA and BiPBA to form ionomers. A
5 wt % polymer solution was prepared using a mixture of
dimethylformamide (DMF)/methanol (95/5, v/v) as solvent (using
pure DMF in the case of BiPBA). The solution was stirred for
24 h and then purged with nitrogen for 1 h before addition of
freshly prepared sodium hydroxide (NaOH) solution (concentra-
tion: 0.05 mol L-1). For each reaction, a calculated amount of
NaOH was added in order to obtain a desired degree of
hydrolysis. The reaction was continued for 24 h, and then the
mixture was precipitated into cold ether (ca. -25 °C). In most
cases, the hydrolyzed polymers precipitated very slowly; they
were collected, redissolved in DMF, and reprecipitated into cold
ether. The finally obtained polymers were dried under vacuum
at 50 °C for at least 3 days. The yields were around 60%. It
should be mentioned that the pure PBA and BiPBA used for
comparison with the ionomers were subjected to the same sample
preparation procedure without hydrolysis, i.e., dissolved in DMF,
collected by precipitation, and dried.

Analysis. The degrees of hydrolysis were difficult to deter-
mine by elemental analysis because of the large side groups in
these polymers, making very small differences in the composition
of the atoms for the partially hydrolyzed samples. 1H NMR
Results and Discussion

Liquid crystalline phases of the hydrolyzed samples were measured by DSC and compared. Figure 1 shows the heating and cooling scan of PBA and some of its ionomers. The results obtained for BIPBA-based ionomers are depicted in Figure 2. In both cases, all samples exhibit liquid crystalline behavior, displaying a liquid crystalline to isotropic transition temperature above the glass transition temperature. As compared with the unhydrolyzed samples, it is clear that the presence of ionic group results in a decrease in the liquid crystalline to isotropic transition temperature. This depression becomes more important as the degree of hydrolysis, i.e., the content of ionic groups, increases. On the other hand, only a slight decrease in \( T_{\mathrm{g}} \) for the ionomers can be noted. The phase transition temperatures are completely reversible upon repeated heating and cooling cycles.

Polarizing microscopy observations confirmed the mesomorphic transition temperatures and showed that for all samples the liquid crystalline phase remained nematic, having a typical schlieren texture when seen between crossed polars. Examples are given in Figure 3 showing the polarized optical micrographs of PBA-0.053Na and BIPBA-0.07Na. It is worthwhile to mention that no difference in the texture could be noticed for the samples having different degrees of hydrolysis.

Table 2 summarizes the results of the DSC measurements by listing the phase transition temperatures and the nematic to isotropic transformation enthalpies. A couple of observations can be made. First, in contrast to the conventional ionomers, whose \( T_{\mathrm{g}} \)'s are known to rise significantly by the presence of ionic aggregates, the \( T_{\mathrm{g}} \)'s of these liquid crystalline ionomers are not increased. This can be explained by two competing factors. In addition to the effects due to the ionic interactions, the partial hydrolysis reaction gives rise to a cleavage of some bulky, mesogenic groups, and the resulting smaller groups should have an effect of reducing the \( T_{\mathrm{g}} \) of the polymer. Another factor which can lead to a decrease in \( T_{\mathrm{g}} \) of ionomers is the presence of water in the samples. We have carefully examined this possibility by doing DSC measurements on samples which were further dried under vacuum at 120 °C for 24 h, and the same results on \( T_{\mathrm{g}} \) and \( T_{\mathrm{d}} \) were obtained within the error of the experimental measurements. Nevertheless, regarding the effects of water, it is interesting to note that for a PBA-0.073Na sample, after being exposed to pure water vapor (100% humidity) for 1 h, a decrease of 4 °C in both \( T_{\mathrm{g}} \) and \( T_{\mathrm{d}} \) was recorded, which arises from a plasticizing effect. Second, it is quite surprising to see that, despite the important depression of \( T_{\mathrm{g}} \), the ionic groups have little effect on the nematic to isotropic transformation enthalpy of these materials. This is particularly evident for the BIPBA-based ionomers; only the temperature range for the mesophase above \( T_{\mathrm{g}} \) is reduced. This is different from the behavior of the liquid crystalline ionomers prepared by partial neutralization of a random copolymer, for which the depression of \( T_{\mathrm{d}} \) is accompanied by a significant decrease in the transformation enthalpy. On the other hand, it can be seen that the decrease in \( T_{\mathrm{d}} \) is greater for the PBA-based ionomers than for the BIPBA-based ionomers at the same expected analysis revealed proportionally increased degrees of hydrolysis, but the values were systematically higher than those expected based on the amounts of NaOH added in the reaction mixtures, due to the error of the NMR measurements as will be indicated later. The results shown in Table 1 are those estimated from thermogravimetric analysis (Perkin-Elmer TGA) by heating the samples to 900 °C and assuming that the residual material was due to sodium, and they are compared with the expected values. The acronyms used for the samples indicate from left to right the liquid crystalline polyacrylate, followed by the expected mole fraction of the sodium salt groups.

Differential scanning calorimetry (DSC) was the technique used to characterize the behavior of liquid crystalline phases. The measurements were performed on a Perkin-Elmer DSC-7 at a heating or cooling rate of 10 °C/min and a sample weight of ca. 15 mg. Glass transition temperatures, \( T_{\mathrm{g}} \), were identified as the midpoint of the step change in the heating scan, and the nematic to isotropic transition temperatures, namely, clearing temperatures \( T_{\mathrm{cl}} \), were taken as the maximum of the melting endothermic peaks. For all the measurements the samples were heated to 140 °C (in the isotropic state) for 10 min before the recorded cooling scan and the following heating scan. Examination of the textures of the samples was performed on a Zeiss Axioskop optical polarizing microscope.

Fourier transform infrared and \( ^1H \) NMR spectroscopies were used to analyze the samples. Infrared spectra were obtained on a Bomen MB-102 FTIR spectrometer at a resolution of 4 cm\(^{-1}\) and from a total of 100 interferograms. NMR spectra were measured on a Bruker AC-300 spectrometer on 3 wt % solutions with DMSO-\( d_6 \) as solvent; a 90° pulse was used.

<table>
<thead>
<tr>
<th>Table 1. Degrees of Hydrolysis of the Samples</th>
</tr>
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<tbody>
<tr>
<td>sample</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>PBA-0.025Na</td>
</tr>
<tr>
<td>PBA-0.053Na</td>
</tr>
<tr>
<td>PBA-0.073Na</td>
</tr>
<tr>
<td>PBA-0.08Na</td>
</tr>
<tr>
<td>BIPBA-0.026Na</td>
</tr>
<tr>
<td>BIPBA-0.07Na</td>
</tr>
<tr>
<td>BIPBA-0.09Na</td>
</tr>
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</table>

Figure 1. DSC Thermograms of (1) PBA, (2) PBA-0.025Na, (3) PBA-0.053Na, and (4) PBA-0.078Na. A: heating scan. B: cooling scan.
contents of ionic groups. But because of the uncertainty in the determination of the degrees of hydrolysis, a clear comparison cannot be made.

Table 2. Phase Transition Temperatures and Enthalpies of the Samples As Determined by DSC

<table>
<thead>
<tr>
<th>sample</th>
<th>( T_v, ^\circ C )</th>
<th>( T_{ab}, ^\circ C )</th>
<th>( \Delta H_{ab}, J/g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBA</td>
<td>30</td>
<td>122</td>
<td>0.92</td>
</tr>
<tr>
<td>PBA-0.025Na</td>
<td>28</td>
<td>106</td>
<td>0.90</td>
</tr>
<tr>
<td>PBA-0.053Na</td>
<td>25</td>
<td>90</td>
<td>0.78</td>
</tr>
<tr>
<td>PBA-0.073Na</td>
<td>24</td>
<td>72</td>
<td>0.77</td>
</tr>
<tr>
<td>PBA-0.09Na</td>
<td>22</td>
<td>65</td>
<td>0.75</td>
</tr>
<tr>
<td>BiPBA</td>
<td>39</td>
<td>117</td>
<td>1.56</td>
</tr>
<tr>
<td>BiPBA-0.025Na</td>
<td>38</td>
<td>117</td>
<td>1.60</td>
</tr>
<tr>
<td>BiPBA-0.07Na</td>
<td>37</td>
<td>107</td>
<td>1.51</td>
</tr>
<tr>
<td>BiPBA-0.09Na</td>
<td>37</td>
<td>88</td>
<td>1.54</td>
</tr>
</tbody>
</table>

The above results clearly demonstrate that the alkaline hydrolysis of liquid crystalline polyacrylates is successful in producing side-chain liquid crystalline ionomers, and their mesophase behavior can be systematically altered by changing the content of ionic groups. What follows is a qualitative explanation for the observed depression of the nematic to isotropic transition temperature with the content of ionic groups. As is familiar, the most important feature of ionomers is the formation of the multiplets, each of which is an aggregate of several ion pairs and contains only the ionic material. The polymer chains anchored to the ionic aggregates have a reduced mobility and fewer available conformations. In the case of the liquid crystalline ionomers investigated here, although the flexible spacer linking the polymer chain and the mesogenic group is relatively long, significant coupling interactions between these two components exist. Keeping this in mind, it is easy to picture that the ionic aggregates disturb the local conformations of the polymer chains surrounding them, which would distort the local nematic order and increase the nematic elastic energy. Consequently, the liquid crystalline phase is less stable and the polymer becomes isotropic at lower temperatures. Obviously, the greater the ion content, the greater the disturbing effect on the nematic order, and more important the depression of the transition temperature. On the basis of the above analysis, it could be expected that all the factors which determine the characteristics of the ionic aggregates (e.g., strength size) would influence the liquid crystalline behavior. These factors include, in addition to ion content, electrostatic interactions between ion pairs, polymer chain flexibility, and steric effects.

Now, let us take a closer look into the alkaline hydrolysis reaction. The hydrolysis of BiPBA, which contains a biphenyl moiety in the side group, is quite straight, since there is only one alkyl ester. Confirmed by infrared and \(^1H\) NMR spectra of the ionomers, the reactions resulted in sodium salts of acrylic acid. Here we focus our attention on the hydrolysis of PBA, for which the situation apparently is more complex. PBA bears a phenyl benzoate moiety in the side group and thus possesses two types of esters: alkyl ester and phenyl ester. The question is whether the hydrolysis reaction resulted in the sodium salt of acrylic acid or the sodium salt of benzoic acid, or a mixture of both.

NMR analysis on the PBA-based ionomers clearly indicates that the hydrolysis of esters only occurred for the phenyl ester groups, giving rise to a sodium salt of benzoic acid. The structure of these ionomers is shown in Figure 4. This conclusion was reached by comparing the ratios of the peak area of the protons in the spacer group, i.e., the alkyl chain linking the chain backbone and the mesogenic group, to the peak area of the protons belonging to the chain backbone; these ratios, within the error of the measurements, remained constant for all the samples having different degrees of hydrolysis. It can be clearly seen that the number of protons in the cyano phenyl group decreases with respect to the number of protons in the other parts of the molecule. This is illustrated in Figure 4 where the \(^1H\) NMR spectra of PBA and some of its ionomers in DMSO-\(d_6\) are shown. The protons of interest are identified on the chemical structure of the ionomers, and their peak assignments are indicated in the figure. It can be seen that the peak area of H-c (in the cyano phenyl group) decreases continuously with respect to the peak area of H-a (in the benzoate group) as the ion content increases; i.e., there are less and less cyano phenyl groups in the resulting ionomers. This change in the NMR spectra...
is directly proportional to the change in the content of ionic groups as revealed by Figure 5, which shows the plot of the nematic to isotropic transition temperature versus the ratio of the peak areas of H-a to H-c. The transition temperature decreases linearly as this ratio increases. However, this ratio does not equal unity for pure PBA, implying the error when using these peaks to calculate the absolute values of the degrees of hydrolysis. One possible source for the error could be the different relaxation times of these protons. Also in Figure 4 it is interesting to note the new signal which appears at about 3.7 ppm in the spectra of the ionomers; the peak intensity increases with the content of ionic groups. This peak can be assigned to H-1' of the methylene groups in the spacer which neighbor the ionic groups, due to a changing shielding effect induced by the presence of the sodium salt groups.

The formation of the sodium salt of benzoic acid for the hydrolysis of PBA can also be observed from the infrared spectra shown in Figure 6. This is best revealed by the change of the 762-cm-1 band which is attributed to the out-of-plane bending of the carbonyl group of the benzoate moiety. For the ionomers the presence of the sodium salt group (-COO-Na+) induces a shift of the 762-cm-1 band to higher frequencies, and this can be seen even in the spectrum of PBA-0.025Na, where a shoulder appears at 770 cm-1 which is absent for PBA. This shoulder becomes more prominent when the content of ionic groups increases.

The changes in intensity of the 1103-cm-1 band, which is absent in the spectrum of BiPBA and hence could be attributed to the phenyl ester groups, is another consequence of the presence of the ionic groups in these ionomers. Actually, it is not surprising to find the highly selective alkaline hydrolysis of PBA to form the sodium salt of benzoic acid. This can be understood by examining the reactivity of the two types of esters present in the polymer structure. A phenyl ester is known to be more reactive than an alkyl ester in general, and in this particular case, the alkaline hydrolysis is proceeded via a saponification reaction so that the hydrolysis of the phenyl ester forms a much better living oxanion, favoring its reaction. On the other hand, the steric effect is one other important factor. The steric hindrance is obviously much stronger for the alkyl ester groups, reducing their reactivity. This steric effect is also manifested in the alkaline hydrolysis of BiPBA, for which the reactions were much slower than the reactions of PBA.

Conclusion

Alkaline hydrolysis of liquid crystalline polyacrylates is shown to be effective in producing side-chain liquid crystalline ionomers. For the polyacrylate containing a phenyl benzoate moiety in the mesogenic side group the hydrolysis by sodium hydroxide occurs at the phenyl ester.
groups and results in the sodium salt of benzoic acid, as revealed by $^1$H NMR and infrared analyses; the reaction is easy to complete and produces a content of ionic groups which is proportional to the amount of NaOH used in the reaction. For the polyacrylate containing a biphenyl moiety in the side group, the hydrolysis reaction is more difficult to complete and results in the sodium salt of acrylic acid. All obtained ionomers display liquid crystalline (nematic) phases, but the liquid crystalline to isotropic transition temperature is depressed by the presence of ionic aggregates in these materials; and the greater the ion content, the greater this depression. On the other hand, ionic aggregates have little effect on the liquid crystalline to isotropic transformation enthalpy and the glass transition temperature, which is particularly evident for the ionomers prepared from the polyacrylate bearing the biphenyl side group. It is expected that the results from this investigation will also apply, in general, to the alkaline hydrolysis of other liquid crystalline polyacrylates as well as liquid crystalline polymethacrylates.

These new liquid crystalline ionomers, with continuously changing nematic to isotropic transition temperature, are used in our laboratory to systematic investigations on the macroscopic orientation of the mesogenic groups under different aligning fields. The results will be reported later.

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References and Notes

(9) Calculations based on these two peaks resulted in degrees of hydrolysis ranging from 11.2 to 29.8% for the PBA ionomers.