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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 crystalline 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 polyacrylate 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 transformation enthalpies as well as the glass transition temperatures of these new materials, in particular for ionomers based on the polyacrylate containing a biphenyl moiety in the side group.

Introduction

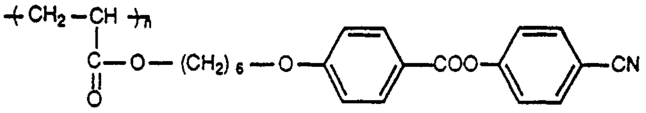
Research and development of side-chain liquid crystalline polymers (LCPs) and ion-containing polymers, namely, ionomers, are two distinct areas of polymer science. Nevertheless, an ion-containing polymer displaying liquid crystalline phases is obviously of great interest for both basic and applied studies. 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 inomers 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 LCP containing ionic charge. As for Blumstein and coworkers,[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 shown[4] that partial neutralization of a copolymer obtained from a mesogenic methacrylate monomer and methacrylic acid comonomer resulted in ionomers exhibiting liquid crystalline phases.

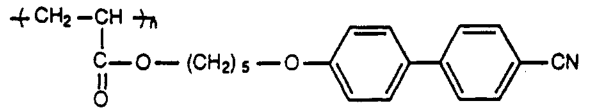
In the present study, we prepared side-chain liquid crystalline ionomers through direct alkaline hydrolysis. To demonstrate the utility of this method, two polyacrylates bearing representative mesogenic side groups, namely, phenyl benzoate and biphenyl moieties, were used. Alkaline hydrolysis is a known method for obtaining conventional acrylate or methacrylate ionomers;[5] 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 microstructure without changing other structural parameters.

Experimental Section

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



PBA



BiPBA

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 ($M_w/M_n = 1.54$), and the sample with the biphenyl moiety in the side group, referred to as BiPBA, has a M_n of ca. 79 000 ($M_w/M_n = 1.78$). 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 (concentration: 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 90 °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 determine 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. ^{1}H NMR

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Table 1. Degrees of Hydrolysis of the Samples

sample	expected, %	estimated, %
PBA-0.025Na	2.5	2.9
PBA-0.053Na	5.3	4.0
PBA-0.073Na	7.3	6.6
PBA-0.09Na	9.0	8.4
BiPBA-0.025Na	2.5	4.9
BiPBA-0.07Na	7.0	9.4
BiPBA-0.09Na	9.0	12.1

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 TG2) by heating the samples to 900 °C and assuming that the residual mateial 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_g's, were identified as the midpoint of the step change in the heating scan, and the nematic to isotropic transition temperatures, namely, clearing temperatures T_{cl}'s, 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 texture of the samples was performed on a Zeiss Axioskop optical polarizing microscope.

Fourier transform infrared and ^{1}H 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.

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_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_g's are known to rise significantly by the presence of ionic aggregates, the T_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_g of the polymer. Another factor which can lead to a decrease in T_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_g and T_{cl} 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_g and T_{cl} was recorded, which arises from a plasticizing effect. Second, it is quite surprising to see that, despite the important depression of T_{cl}, 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_g is reduced. This is different from the behavior of the liquid crystalline ionomers prepared by partial neutralization of a random copolymer,[4] for which the depression of T_{cl} is accompanied by a significant decrease in the transformation enthalpy. On the other hand, it can be seen that the decrease in T_{cl} is greater for the PBA-based ionomers than for the BiPBA-based ionomers at the same expected

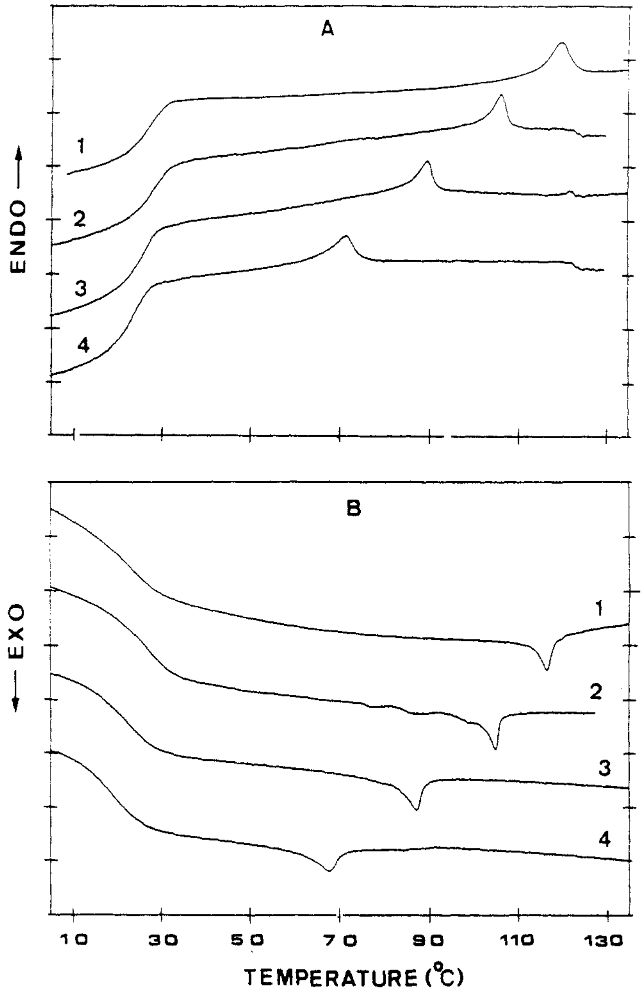


Figure 1. DSC Thermograms of (1) PBA, (2) PBA-0.025Na, (3) PBA-0.053Na, and (4) PBA-0.073Na. A: heating scan. B: cooling scan.

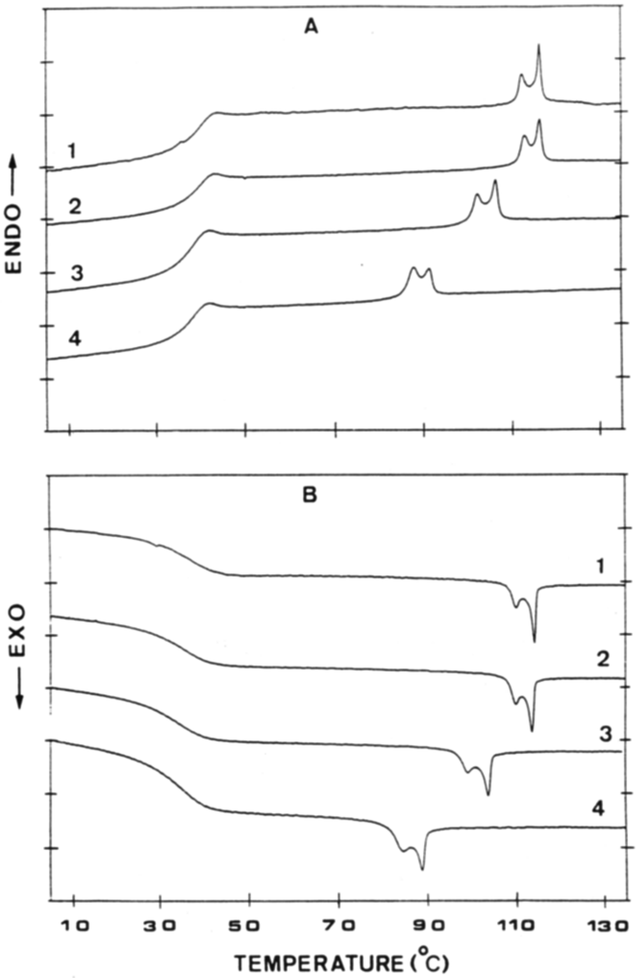
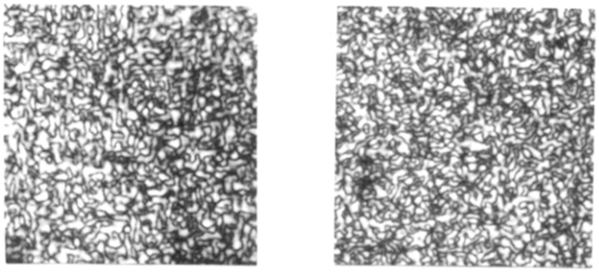


Figure 2. DSC thermograms of (1) BiPBA, (2) BiPBA-0.025Na, (3) BiPBA-0.07Na, and (4) BiPBA-0.09Na. A: heating scan. B: cooling scan.



a b

Figure 3. Polarized optical micrographs of (a) PBA-0.053Na and (b) BiPBA-0.07Na, displaying the typical nematic texture. Magnification: 250×. The samples were first kept at T_{cl} + 20 °C for 10 min and then cooled to room temperature.

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

sample	T_g, °C	T_{cl}, °C	ΔH_{cl}, J/g
PBA	30	122	0.92
PBA-0.025Na	28	106	0.90
PBA-0.053Na	25	90	0.78
PBA-0.073Na	24	72	0.77
PBA-0.09Na	22	65	0.75
BiPBA	39	117	1.56
BiPBA-0.025Na	38	117	1.60
BiPBA-0.07Na	37	107	1.51
BiPBA-0.09Na	37	88	1.54

contents of ionic groups. But because of the uncertainty in the determination of the degrees of hydrolysis, a clear comparison cannot be made.

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,[8] 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.[8]

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. Cinfirmed by infrared and ^{1}H 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 cyanophenyl group decreases with respect to the number of protons in the other parts of the molecule. This is illustrated in Figure 4 where the ^{1}H 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 cyanophenyl 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 cyanophenyl groups in the resulting ionomers. This change in the NMR spectra

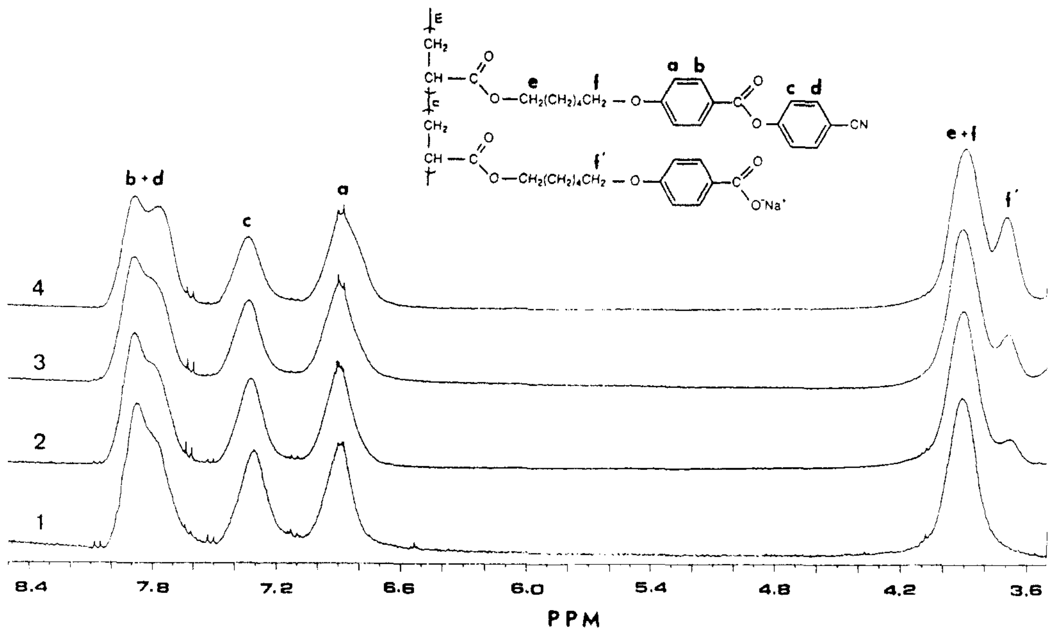


Figure 4. 300-MHz ^{1}H NMR spectra in DMSO-d_6 of (1) PBA, (2) PBA-0.025Na, (3) PBA-0.053Na, and (4) PBA-0.093Na.

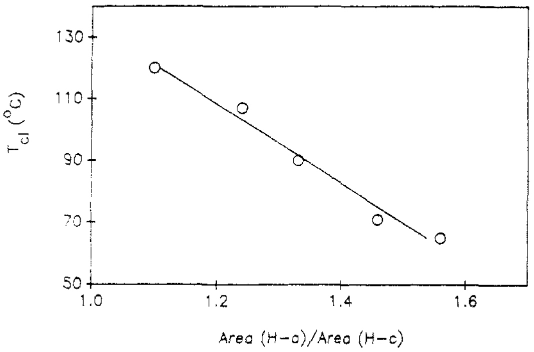


Figure 5. Nematic to isotropic transition temperature vs ratio of the peak areas of H-a to H-c of PBA and its ionomers. Peak assignments and identification of the protons are indicated in Figure 4.

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.[9] 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-f′ 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.

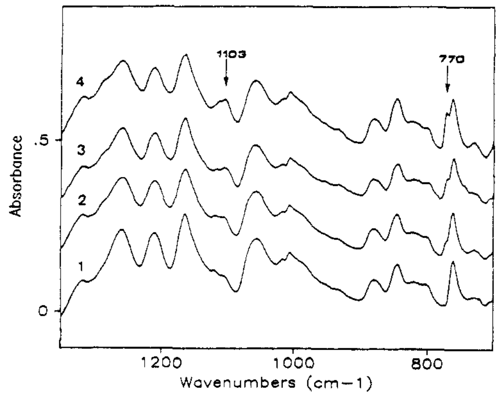


Figure 6. Infrared spectra, in the 700–1350-cm^{-1} region, of (1) PBA, (2) PBA-0.025Na, (3) PBA-0.053Na, and (4) PBA-0.073Na.

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[5] 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 ont 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 for systematic investigations on the macroscopic orientation of the mesogenic groups under different aligning fields. The results will be reported later.

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