Polymer Bulletin 31, 645–649 (1993)

Polymer Bulletin

An easy way of preparing side-chain liquid crystalline ionomers

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SUMMARY

A simple synthesis method is shown to be effective to produce side-chain liquid crystalline ionomers. The method is based on random copolymerization of a methacrylate monomer bearing a mesogenic group with the methacrylic acid as comonomer; the copolymer is partially neutralized to various degrees to form ionomers. Differential scanning calorimetry measurements show that the liquid crystalline behavior is modified by the presence of ionic aggregates, which is reflected, in the present case, by a depression of the nematic to isotropic transition temperature and enthalpy.

INTRODUCTION

It is of obvious interest to explore ion-containing liquid crystalline polymers (LCPs) which combine the specific features of both ionomers and LCPs. Recently, in the context of our studies of the macroscopic order in side-chain LCPs (1,2), we are interested in using LC ionomers as a model system to carry out systematic investigations on the effects of the intrinsically oriented-microstructure on the macroscopic order creation under different aligning fields. The main advantage of using these polymers is that the mesophase behavior can readily be modified by the presence of ionic aggregates.

Very few studies on LC ionomers have been reported so far (3,4), in which some synthesis methods were proposed. In this paper, we present some preliminary results showing a very convenient and effective way of preparing side-chain LC ionomers. The method is based on random copolymerization of a methacrylate monomer bearing a mesogenic group with the methacrylic acid comonomer, followed by neutralization of the acid groups in the LC copolymer.

EXPERIMENTAL

The mesogenic monomer [I], i.e., 4-cyanophenyl-4-(6-methacryloyloxy)hexyloxy)benzoate, was prepared as described in the literature (5). For the sake of comparison, a nematic homopolymer was prepared from [I], referred as PBMA. The copolymer investigated, namely PBMA-MAA, was obtained by copolymerization of [I] with the methacrylic acid [II] with a 90/10 mole ratio in the initial feedstock. The polymerization for both PBMA and PBMA-MAA was

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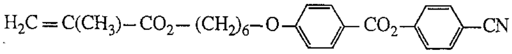
undertaken at 60°C for 24 h. Toluene was used as solvent and 0.5 mol % AIBN as initiator. For purification, the obtained polymers were twice dissolved in chloroform and precipitated in cold (0°C) ethyl ether before being dried under vacuum at 60°C. The concentration of monomer [II] in the copolymer was determined to be about 12 mol % by ^1H n.m.r. spectroscopy (sample dissolved in dimethyl sulfoxide). The number-average molecular weight of the samples, estimated by GPC using polystyrene standards, is about 42,000 g/mol ($M_w/M_n \approx 1.6$).

| I |



| II | $H_2C{=}C(CH_3){-}CO_2H$

To obtain the ionomers, the PBMA-MAA was partially neutralized to various degrees. The neutralization was performed by dissolving 1 wt % copolymer in benzene/methanol (volume ratio 95/5), bubbling dry nitrogen through the solution, and then adding calculated amounts of potassium carbonate in methanol (0.023 mol L^{-1}) into the solution. The formed ionomers were collected and dried under vacuum at 80°C for several days.

The differential scanning calorimetry (DSC) was used to characterize the mesophase behavior of the samples. 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 about 15 mg. Infrared spectra were recorded with a Bomen MB-102 FTIR spectrometer at a resolution of 4 cm^{-1} and from a total of 100 interferograms.

RESULTS AND DISCUSSION

In contrast with PBMA and PBMA-MAA, all neutralized samples are insoluble in common organic solvents such as toluene, chloroform and THF, indicating the existence of strong ionic aggregations in these ionomers. The presence of the neutralizing cation can also be observed from the infrared spectra in Figure 1 for PBMA-MAA and two of its corresponding ionomers, PBMA-MAA-0.5 K and PBMA-MAA-0.7 K (0.5 K and 0.7 K mean neutralization degrees of 50 and 70%, respectively, with potassium cation). Two new bands appear at about 1560 and 1390 cm^{-1} (for the latter band this can be seen from change in the intensity); these are assigned to the asymmetrical and symmetrical COO^- stretching vibrations, respectively (6). And it is clear that the absorbance of both bands increases as the ionization degree increases.

Figure 2 shows the DSC curves, obtained from the second heating scan and the following cooling scan, for PBMA, PBMA-MAA and the two ionomers with 50 and 70% acid groups neutralized, respectively. Two observations can be made. Firstly, in comparison with the homopolymer, the random incorporation of the methacrylic acid units in the copolymer results in an increase in the glass transition temperature T_g, which is due to the intermolecular hydrogen bonding interactions formed between the acid groups, and the disappearance

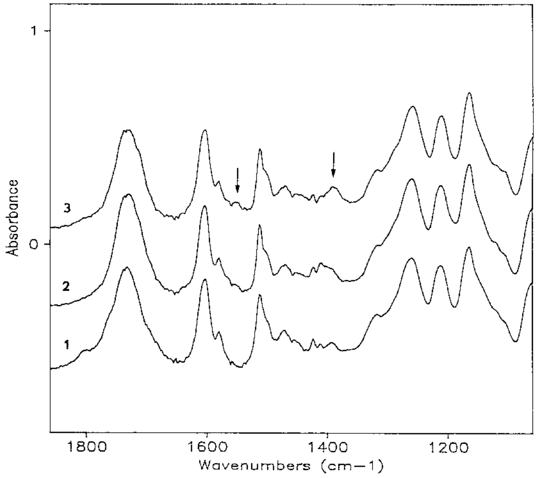


Figure 1
Infrared spectra, in the 1060-1860 cm^{-1} region, of (1) PBMA-MAA, (2) PBMA-MAA-0.5K, and (3) PBMA-MAA-0.7K.

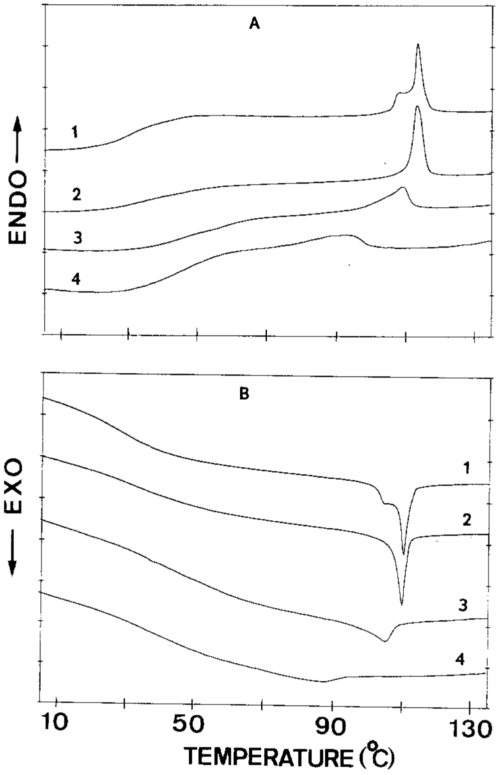


Figure 2
DSC thermograms of (1) PBMA, (2) PBMA-MAA, (3) PBMA-MAA-0.5K, and (4) PBMA-MAA-0.7K.
A: second heating scan
B: following cooling scan

of the side peak in the nematic to isotropic transition zone without changing the maximum transition temperature, i.e., the clearing temperature T_{cl}. Secondly, the presence of the potassium cation in the ionomers leads to a further increase in T_g as compared to the copolymer, which is due to stronger ionic interactions, and a significant depress of T_{cl}. It can be seen that T_{cl} decreases with increasing the degree of neutralization, that is, the higher the ion content in the polymer, the lower the nematic to isotropic transition temperature. No notable changes in the DSC curves could be observed for subsequent heating and cooling; the transitions were reversible.

Table 1 Phase transition temperatures and enthalpies of the samples

polymer	ionization deg, %	T_g, °C	T_{cl} , °C	ΔH_{cl} , J/g
PBMA		31	113	2.9
PBMA-MAA		37	113	2.7
PBMA-MAA-0.3K	30	48	111	1.6
PBMA-MAA-0.5K	50	50	109	1.1
PBMA-MAA-0.7K	70	46	94	0.9
PBMA-MAA-0.8K	80	53	80	0.3

The results of the DSC measurements are summarized in Table 1, in which are given the phase transition temperatures as well as the nematic to isotropic transformation enthalpies ΔH_{cl} for different samples. As compared to the copolymer, the depression of T_{cl} with the ion content is accompanied by a decrease in the transition enthalpy. This clearly indicates that the presence of ionic aggregates in liquid crystalline methacrylate polymers seriously weakens the ordered nematic structure, and less thermal energy is needed for isotropization of the polymer. It should be mentioned that the sample neutralized to 80% displays only a very weak nematic to isotropic transition endotherm, and above this degree of neutralization no mesophase transition could be observed.

To summarize, the example given in this paper illustrates an easy and effective method of preparing side-chain liquid crystalline ionomers. By changing a number of parameters, e.g. mesogenic group, neutralizing cation and its content, ionomers exhibiting different mesophase behaviors can be obtained. The LC ionomers are interesting polymers and will be proved useful for studies of macroscopic orientation in LCPs. Works are in progress in our laboratory in this field.

ACKNOWLEDGMENT

Financial support from the Natural Sciences and Engineering Research Council of Canada and FCAR of the Province of Quebec is acknowledged.

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Accepted October 13, 1993 K