

Studies on Salts of Amine-Containing Polymers with Benzoic Acids. III. Poly(*N,N*-dimethylaminoethyl methacrylate-*g*-polyethylene) with Benzoic Acids

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Received 14 July 1999; accepted 31 January 2000

ABSTRACT: Poly(*N,N*-dimethylaminoethyl methacrylate) [poly(DMAEMA)] was grafted onto a commercial polyethylene film by means of γ -irradiation, and the grafted films were reacted with various liquid-crystal-forming benzoic acids. When polymeric salts consisting only of poly(DMAEMA) and the benzoic acids were heated, dissociation of salts was observed, but with poly(DMAEMA) grafted onto polyethylene films, salt dissociation or crystallization of dissociated acids could be avoided, and interesting morphologies, including liquid-crystal phases, were observed for the systems of benzoic acids–poly(DMAEMA-*g*-polyethylene). © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 972–978, 2000

Key words: benzoic acids; grafted polyethylene film; poly(*N,N*-dimethylaminoethyl methacrylate); polymeric salts

INTRODUCTION

An important method for obtaining functional polymers is chemical modification of common polymers by the reaction of compounds with different functionalities. This method has an advantage over synthesis of monomers with desired functional groups, which usually involves laborious synthetic processes. Commonly, a

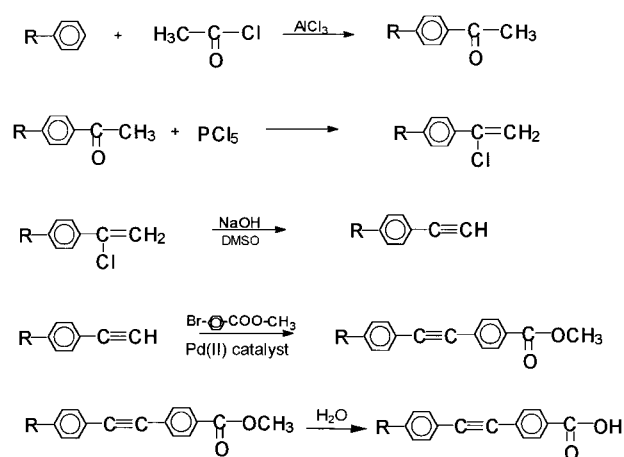
great number of chemical modifications of polymers have been investigated, and the majority of investigations have been concerned with the introduction of functional groups through covalent bonding.^{1,2} However, little has been studied on the introduction of functional groups through noncovalent bonding, such as hydrogen and ionic bonds. Recently, this field has been attracting much interest, especially in the area of side-chain liquid polymer synthesis. Kato and Fréchet³ have reported a liquid-crystal polymer consisting of a benzoic-acid-containing polymer and a mesogenic pyridine derivative combined by hydrogen bonding. Malik et al.⁴ have also reported a series of polymer liquid crystals formed by hydrogen bonding between the polymers and the mesogens. This field was de-

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Contract grant sponsor: DGAPA-UNAM; contract grant number: IN-102195.

Journal of Applied Polymer Science, Vol. 78, 972–978 (2000)
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scribed in the recent review article by Bazuin.⁵ When polymeric composites consisting of host polymers and guest functional compounds are desired, the presence of certain chemical interactions such as salt formation will increase compatibility, and the concentration of the guest molecules can be increased to emphasize their functionality. There are many studies on polymeric salts known as ionomers, which consist of acid polymers and metal ions.⁶ However, in comparison with metallic salts, relatively little has been reported on polymeric salts consisting of amine polymers with organic acids, unlike with acid polymers. The authors of the present study have previously reported systems consisting of poly(*N,N*-dimethylaminoethyl methacrylate) [poly(DMAEMA)] and various benzoic acids.^{7,8} The morphology of the mixed systems differed considerably depending on the type of benzoic acid. In the cases of alkoxybenzylidene aminobenzoic acids, LC particles were formed in the systems, but the acids were completely mixed with poly(DMAEMA), losing the LC phases by repeated heating and cooling.⁸ Mixed polymeric systems containing benzoic acids having various functional groups are interesting materials to study because the benzoic acid derivatives can be readily synthesized and readily miscible with commercially available amine-containing polymers such as poly(DMAEMA)—poly(*N,N*-dimethylaminopropyl methacrylamide)—and their copolymers, and their chemical and physical properties can be easily controlled by the type and amount of the benzoic acids. Polymeric salts might have some disadvantages, such as lack of mechanical strength, brittleness of films, hygroscopic nature, and so forth. In this work, in order to see the effect of hydrophobic polymer films on polymeric salt films, γ -ray-induced grafting of poly(DMAEMA) onto a commercial polyethylene



Scheme 1. Synthetic route of alkyltolan carboxylic acids.

(PE) film was carried out, and several different benzoic acid derivatives were added to the grafted films. The results on the characterization and some behaviors of the product films are reported in this article.

EXPERIMENTAL

The benzoic acids, *p*-ethoxy, *p*-*n*-butoxy, and *p*-*n*-octyloxy benzoic acids, hereafter abbreviated as EOA, BOA, and OOA, respectively, were supplied by Aldrich, and they were used as received. Preparation of tolan carboxylic acids was done with methods⁹ that used the reactions shown in Scheme 1. For *p*-1-decynylbenzoic acid (DYA) the preparation was by the reaction of 1-decyne with *p*-bromomethylbenzoate in a mixture of triethylamine and pyridine using bis(triphenylphosphine)-palladium(II) chloride, triphenylphosphine, and copper(I) iodide, followed by hydrolysis of the ester. They were purified by recrystallization and confirmed by NMR and IR

Table I Thermal Transitions of Benzoic Acids Determined by DSC

<i>p</i> -X-C ₆ H ₄ -COOH X=	Abbreviation	Phase Transitions (°C)	Sublimation (°C ^a)
C ₂ H ₅ -O-	EOA	199(n) 200(i)	185
C ₄ H ₉ -O-	BOA	148(n) 161(i)	190
C ₈ H ₁₇ -O-	OOA	101(s) 108(n) 147(i)	250
C ₄ H ₉ -C ₆ H ₄ -C≡C-	BTA	219(n) 253(i)	260
C ₈ H ₁₇ -C≡C-	DYA	83(n) 113(i)	270
C ₅ H ₁₁ -C ₆ H ₄ -C≡C-	PTA	159(s) 176(n) 261(i)	266

^a From DSC and TGA.

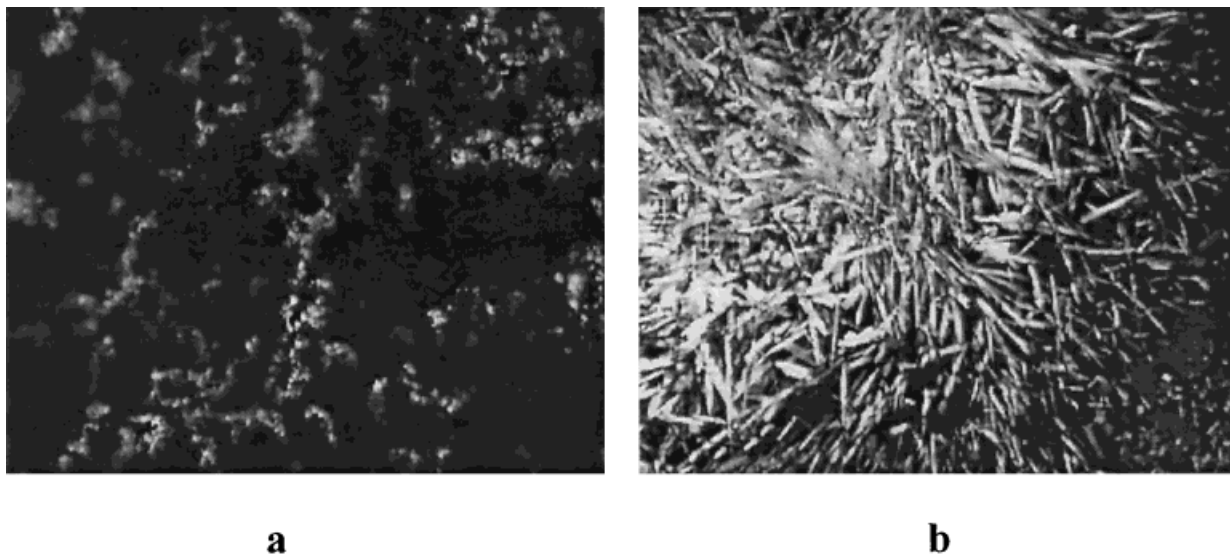


Figure 1 Polarized optical micrographs of poly(DMAEMA)/OOA (molar ratio: 0.8): (a) casted film, room temperature; (b) heated to 190°C and cooled to room temperature.

spectroscopy. Their thermal characteristics are given in Table I.

The PE film (LDPE) was a PEMEX product melting at 115°C and with thickness of 0.07 mm and a crystallinity of 62%. The film was irradiated in air to form peroxides by γ -ray (Co^{60} Gamma Beam 651 PT) irradiation, and it was placed into an ampoule containing a benzene solution of DMAEMA, and the ampoule was sealed off in a vacuum. The ampoules were heated for lengths in hours at temperatures above 45°C, at which the peroxide formed in the PE film breaks to form initiator radicals. The grafting yield was determined from the weight increase. The grafted films were then dipped in a methanol containing an excess of the benzoic acid, and after 24 h the films were washed with methanol, dried in a vacuum at room temperature, and weighed. The percentage of salt formation was calculated from the weight difference. The swelling of the grafted films in methanol was determined gravimetrically by weighing samples in methanol at timed intervals until constant weights were reached.

Benzoic acids salts of poly(DMAEMA) were prepared for comparison purposes simply by mixing the two in methanol, followed by evaporating the methanol.

A polarized optical microscope, Olympus BHC, fitted with a Leitz hot stage was used for microscope observations. X-ray diffractometry was performed using a Siemens D-500 diffractometer

with $\text{Cu K}\alpha$ radiation of 1.5406 Å. Differential scanning calorimetry (DSC) was carried out using a TA Instrument calorimeter (Model 910).

RESULTS AND DISCUSSION

Salt Formation of Benzoic Acids with Poly(DMAEMA)

X-Ray diffraction patterns of the poly(DMAEMA) containing the tolan carboxylic acids and DYA showed that the mixtures were amorphous when the acid concentration mixed with the polymer did not exceed 0.8 (mol/mol). In the cases of EOA and BOA the materials were also amorphous when the acid concentration did not exceed 0.5 and 0.8 (mol/mol), respectively, of DMAEMA, and beyond these concentrations it seemed that the excess acid existed as free-acid microcrystals dispersed in the amorphous polymer. The FTIR spectra of the mixtures of poly(DMAEMA) with BOA clearly indicated salt formation as the absorption band because of the carbonyl groups of the acid dimers at around 1290 cm^{-1} disappeared by proton transfer to the tertiary amine of the polymer, and the carbonyl peak of the dimeric acid at 1674 cm^{-1} shifted to 1698 cm^{-1} and weakened because of the salt formation with the tertiary amine group.

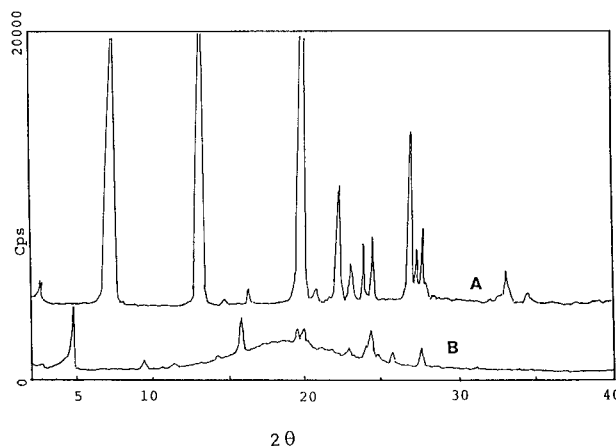


Figure 2 X-ray diffraction patterns of (a) OOA and (b) salt of OOA with poly(DMAEMA) (molar ratio = 0.8).

The polarized optical microscope observations for a film containing 80 mol % of BOA revealed that the film contained a small amount of crystalline particles of the free acid. On heating to a temperature of 190°C, the film became totally amorphous, and on cooling, the acid that was separated from the poly(DMAEMA) crystallized, creating a film covered with BOA crystals and indicating that the dissociation of salt was irreversible. In the case of EOA, when the film was heated to 200°C to melt and then cooled, no crystallization was observed because of sublimation of EOA, which separated from the host polymer. However, in the case of film containing 80 mol % of OOA, polarized optical microscope observation revealed the film consisted of crystalline and amorphous parts [Fig. 1(a)], and the system suddenly changed its texture at 73°C, followed by the appearance of fine needle crystals of the OOA that had separated from the host polymer. The crystals started to melt at 83°C (the melting point of pure OOA is 101°C), followed by formation of a nematic mesophase that became an isotropic phase at 143°C. The liquid crystal of OOA has been reported in the literature.^{10,11} On heating to a temperature of 190°C, the material became totally amorphous, but on cooling, all OOA that had separated from the host polymer crystallized, making a film filled with colorful large crystals and indicating that the dissociation of salt took was irreversible, as shown in Figure 1(b). It seems that on evaporation some benzoic acid salts of poly(DMAEMA) crystallize solvents from their solutions. Previously, polymeric salts with different morphologies—amorphous, spherulite, and

crystalline lumps, depending on the film-forming conditions—were obtained for a system of poly(DMAEMA)-*p*-1-hydroxycyclohexylethynylbenzoic acid,⁷ and it seems that OOA can convert an amorphous polymer, poly(DMAEMA) into a partially crystalline polymer. The X-ray diffractometry (Fig. 2) showed the film's crystallinity to be approximately 25%, which is not because of the OOA aggregates dispersed in the amorphous host polymer.

The DSC of the mixtures of alkoxybenzoic acids showed an intense endotherm at around 200°C, which corresponded to sublimation of the acids. A small ambiguous endotherm at around 100°C results from the dissociation of the acids. Thermal gravimetric analysis of these *p*-alkoxybenzoic acids showed sublimation beginning at temperatures of 185°C and 190°C for EOA and BOA, respectively. Therefore, the endotherm appearing at 200–250°C in DSC is due to the sublimation of the acids. The sublimation temperatures of these benzoic acids, determined by the DSC are shown in Table IH.

Salt Formation of Benzoic Acids with Poly(DMAEMA) Grafted onto PE

Radiation-induced grafting of DMAEMA onto LDPE was reported previously.¹ The FTIR spectra of these grafted films containing benzoic acids also indicated a salt formation similar to the cases of poly(DMAEMA) with benzoic acids, as the peaks of the acid carbonyl group at 1678 and 1290 cm^{-1} disappeared for the films. The salt formation of benzoic acids with the grafted poly(DMAEMA) depended on the grafting conditions, such as monomer concentration, temperature, preirradiation dose, and so forth. Table II shows the variation in salt formation depending on the grafting conditions in the case of BTA. The salt formation yield was different in the two experiments, the result of swelling of the grafted polymers in methanol, the solvent used for salt formation.

Table II Salt Formation of Butyltolan Carboxylic Acid in Poly(DMAEMA)-*g*-PE

DMAEMA–benzene (v/v)	80/20	60/40
Reaction Temperature	45°C	55°C
Reaction Time	21 h	22 h
Preirradiation Dose	250 kGy	250 kGy
Graft %	105	101
Salt Formation %	23	50
Swelling % in Methanol	47	128

Table III Optical Microscope Observation and DSC Determination for Poly(DMAEMA-*g*-PE) Containing Benzoic Acids

<i>p</i> -X—C ₆ H ₄ —COOH X:	PE- <i>g</i> -DMAEMA		DSC on Heating	Optical Microscope Observation
	(%) Graft	(%) Salt		
PE alone			$T_m = 115$	
Poly(DMAEMA) alone			$T_g \approx 20$	
Poly(DMAEMA)- <i>g</i> -PE) alone	53	0	$T_g = 15-16^\circ\text{C}$ $T_m = 111$	
C ₂ H ₅ O—EOA	50	54	$T_g = 49$ $T_m = 111$	Amorphous. Small amount of dispersed benzoic acid crystals, which melt at 114°C.
C ₄ H ₉ O—BOA	50	14	$T_g = 37$ $T_m = 112$	Small Maltese crosses dispersed in amorphous texture, which disappear at 113°C; on cooling reappear at 83°C.
C ₈ H ₁₇ O—OOA	105	29	$T_g = 30$ $T_m = 113$	Birefringent structure, fading at 110°C, but at 126°C LC phase of acid. At 153°C becomes isotropic. On cooling returns to original structure.
C ₈ H ₁₇ —O—OOA	41.5	24		Texture with brilliant particles, fading at 110°C; becomes less brilliant above 125°C; on cooling from 180°C becomes brilliant again at 65°C.
C ₈ H ₁₇ —O—OOA	206	87		Similar to the above—brilliant particles become smaller at 65°C and lose brightness at 77°C; on cooling brightness reappears.
C ₈ H ₁₇ —C≡C—DYA	56	30	$T_g = 30$ $T_m = 113$	Slightly brilliant particles dispersed in texture; at 80°C become smaller but more brilliant; become amorphous at 110°C; on cooling return to the original texture.
C ₄ H ₉ —Ph—C≡C—BTA	100	50	$T_g = 32.0$ $T_m = 113.2$	Bright particles dispersed; disappear above 80°C; at 104°C system melts, but isolated acid crystals are observed; Cooling makes film opaque because of crystallization of benzoic acid.
C ₄ H ₉ —Ph—C≡C—BTA	105	23		Bright particles dispersed; similar behavior as above; on cooling make transparent film, as original structure.
C ₅ H ₁₁ —Ph—C≡C—PTA	100	45	$T_g = 21$ $T_m = 113.59$	Birefringent with small Maltese crosses; softening at 114°C, and at 157°C film becomes red with same structure as original, and LC starts to melt; on cooling the same texture returns but Maltese crosses do not reappear.

The relationships between the swelling of the grafted polymer films and the grafting conditions were studied. It was found that when the mono-

mer (DMAEMA) concentration was low—that is, when the concentration of the solvent (benzene) was high—the swelling of the PE film in benzene

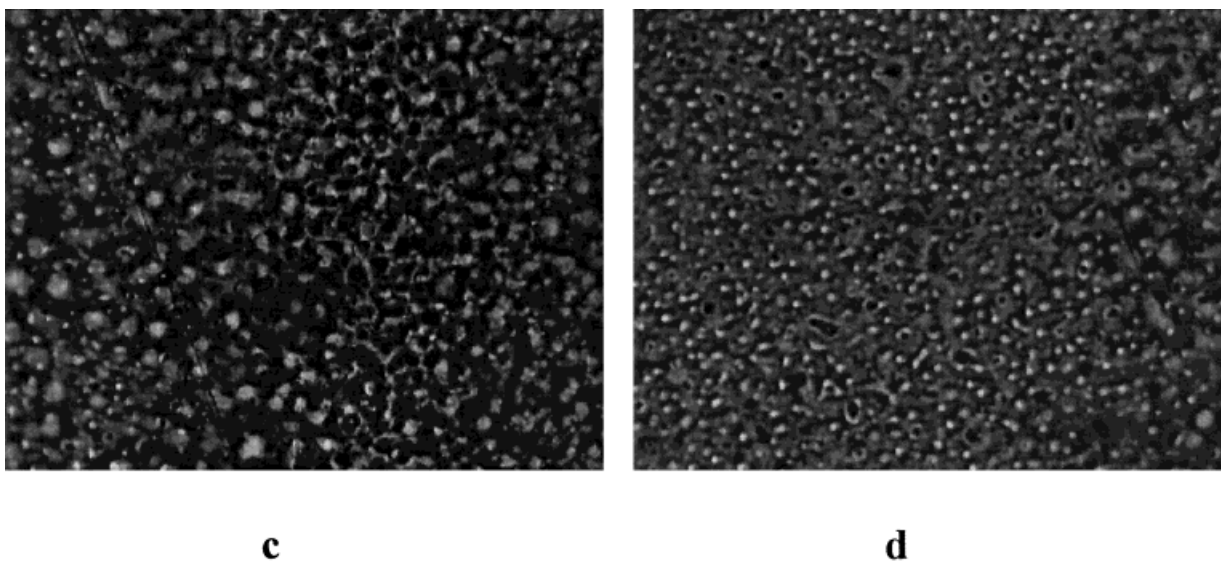


Figure 3 Polarized optical micrograph of poly(DMAEMA)-*g*-PE/OOA system (105% grafted, 29% salt): (c) room temperature, (d) heated to 190°C and cooled to room temperature.

allowed the penetration of the monomer, and the grafting took place inside the PE film. Consequently, methanol, the solvent used for salt formation, swelled the film, increasing the amount of benzoic acids incorporated in the films. When the monomer concentration was high, the PE films did not swell, and the grafting took place on the film surface; therefore, they swelled smaller and smaller amounts of benzoic acids, which were incorporated in the film. When the grafting temperature was increased, the monomer penetrated deep in the PE film, thus increasing swelling. Therefore, it is possible to control the grafting and consequently the amount of salt in the film.

The crystallinity of PE decreases with an increase in grafting, as expected. The PE crystallinity did not decrease further by the addition of EOA, as the salt formation is only in the grafted part of PE film, which became amorphous. The DSC of the grafted systems containing these benzoic acids showed a T_g of poly(DMAEMA) salts in a range from 20°C to 50°C and melting of PE at around 110–113°C, which is slightly lower than the melting point of PE alone, 115°C. The T_g of poly(DMAEMA) is around 20°C, decreased by grafting to 15°C–16°C, and increased with the addition of the benzoic acids, as can be seen in Table III. They decreased with the chain length of the acids, while T_m did not change with the type of the acids. The optical microscope observations are summarized in Table III. In contrast to low-molecular-weight liquid crystals, which

crystallize on cooling, LC polymers with mesogenic groups pass into the glassy state with preservation of the LC structure corresponding to a certain mesophase.^{13,14} This can be applied to the results of this work. With the exception of the case of EOA, the systems showed defined birefringent structure, which are reproducible in repeated heating and cooling. In some cases, such as of BOA and PTA, spherulites in the shape of Maltese crosses were observed. It can be noted that the system of BTA, which possesses a more rigid structure than the other acids, is less miscible with the host polymer system; thus, with the higher acid concentration (50% salt) crystallization of dissociated acid was observed to a certain extent. Figure 3 shows an example microphotograph of the system consisting of poly(DMAEMA)-*g*-PE with OOA. The morphology of the systems with different compositions were similar to each other. In comparison with the corresponding case of poly(DMAEMA) with OOA, no crystallization of the dissociated OOA was observed during heating to 190°C and cooling to room temperature. Thus the grafting of polymeric salts on PE showed an important advantage over the corresponding simple polymeric salts; in the latter case, the acids dissociate from the polymer on heating, and on cooling only the separated acids crystallized, forming a simple mixtures. Figure 4 shows DSC curves for the poly(DMAEMA)-*g*-PE with DYA. Its T_g appears at around 24°C, and the peak at 82°C is not assigned, but the texture became more bright

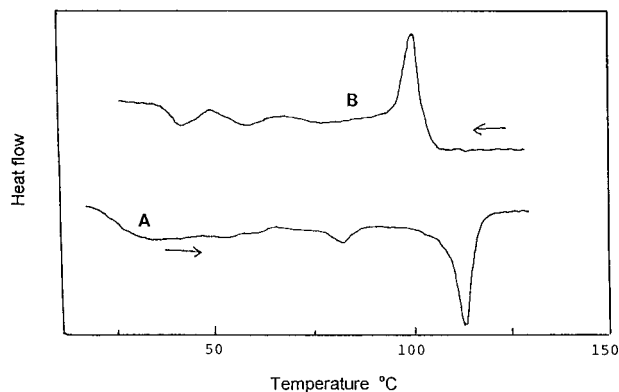


Figure 4 DSC curves of poly(DMAEMA)-*g*-PE/DYA system: (a) heating, (b) cooling.

around this temperature under the polarized microscope observation. DYA alone exhibits its nematic mesophase over the temperature range 83–113°C, but no such phase was observed in the mixture. In the previous study about the case of *p*, *p'*-alkoxybenzylidene aminobenzoic acids mixed with poly(DMAEMA),⁸ the acids separates from the polymer and their nematic phases were formed. In the cases of the mixtures of poly(DMAEMA) with OOA and DYA nematic phases of the separated acids were observed. Therefore, in the case of the salts of the poly(DMAEMA)-*g*-PE with DYA, it seems that the acid does not separate from the host polymer to form its own LC phase. The endotherm peak at 113°C is the melting point of PE, but at this moment the system becomes totally isotropic. On cooling from 125°C, the original texture was reproduced, and the heating–cooling process could be repeated without change in the texture.

It can be concluded from this work that in cases of polymeric salts grafted to PE, the same original textures are reproduced on cooling, and this is the most significant difference between grafted and nongrafted poly(DMAEMA)–benzoic acids salts. The probable reason for this is the affinity of the *p*-substituted groups of benzoic acids to PE, which inhibits the dissociation of salts or more probably prevents the diffusion of the dissociated acid molecules in the host polymer, thus avoiding their

recrystallization and facilitating reformation of the salts. The salts of amine-containing polymers with benzoic acids are interesting and unique materials because a variety of morphologies are produced, depending on the type of benzoic acids and on the conditions of salt formation. It is noteworthy to mention that a totally amorphous polymer, such as poly(DMAEMA), can be converted to partially crystalline polymer by the addition of certain benzoic acids. Further studies with different host polymer films and grafting monomers are in progress.

The authors are greatly indebted to Ma. del Pilar Carreón, Carmen Vázquez, Epifanio Cruz, Leticia Baños and Salvador Ham for their technical assistance.

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