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Studies on salts of amine-containing polymers with benzoic acids

II. Poly(*N*,*N'*-dimethylaminoethylmethacrylate) with alcoxybenzylideneaminobenzoic acids

Margarita Marin [1], **Leticia Baños** [1], **Abel Moreno** [1], **Guillermina Burillo** [2], **Takeshi Ogawa** [1,*]

[1] Instituto de Investigaciones en Materiales, and [2] Instituto de Ciencias Nucleares,
Universidad Nacional Autonoma de Mexico, Circuito Exterior, Ciudad Universitaria,
04510-México, D.F., Mexico

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Summary

The thermal behaviors of various benzoic acids and liquid crystal forming *p*- alcoxybenzylidene-*p*-aminobenzoic acids in poly(N,N-dimethylaminoethylmethacrylate) were investigated. It was found that these liquid crystal forming benzoic acids do not form salts with the dimethylehylamino groups of the host polymer, and formed nematic liquid crystal particles dispersed in the polymer. The melting point of the host polymer decreased from about 200 °C to around 140 °C by the addition of the acids. On heating the mixture the acids were gradually dissolved in the polymer, and totally homogeneous mixtures without liquid crystalline phase were formed.

INTRODUCTION

Mixed systems consisting of polymers and functional organic compounds are interesting topics of investigation, because they have many possible applications in different fields. Typical examples include mixtures of liquid crystals with polymers, and materials for second order nonlinear optics, etc. When the host polymers and the guest molecules have certain chemical interactions, such as salt formation or ionic interactions, the concentration of guest molecules in the polymer can be increased due to the increased miscibility. The behaviors of the guest molecules in the host polymers in such systems are expected to be more complex than those in the cases of mixed systems without chemical interactions, and their morphology will differ depending on the type of guest molecules. Very little has been studied on the polymeric mixed systems consisting of basic polymers with organic acids. Basuin, et al.[1] have recently reported a system consisting of poly(4-vinylpyridine) and a di-n-alkoxy biphenyl mesogen functionalized by a carboxilic acid group. The present authors reported previously[2] that the morphology and thermal behaviors of poly(N,N-dimethylaminoethymetacrylate), poly-DMAMA, mixed with various ben-

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[*] Corresponding author

zoic acids vary drastically depending on the type of the added benzoic acids, and in many cases the thermal properties of the mixtures differed completely from those of the two alone before mixing.

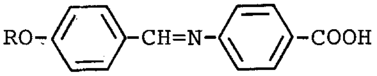
In this work a series of liquid crystal forming benzoic acids, *p*-alcoxybenzylidene-*p*-aminobenzoic acids, Cn-BBA, were mixed with poly-DMAMA, and the morphology and thermal properties of these mixtures were investigated. In order to see the interaction between the benzoic acids and poly-DMAMA, a thermal study of mixtures of poly-DMAMA with various simple benzoic acids was also carried out. The results are reported in this paper.

EXPERIMENTAL

MATERIALS

The poly-DMAMA was prepared by polymerization of N,N-dimethylaminoethylmethacrylate (Aldrich) in benzene (50% v/v) using 2.2'-azobisisobutyronitrile (0.02M) at 50 °C. The poly-DMAMA obtained was purified by reprecipitation in hexanes. The number average molecular weight was found to be 96,000 g/mol measured by osmometry at 40 °C in ethanol. The simple benzoic acids (Aldrich) were purified by dissolving in aqueous sodium hydroxide solution, and after filtering insoluble matters, they were reprecipitated in hydrochloric acid. The Cn-BBA were prepared by the reaction of *p*-alcoxybenzaldehydes with *p*-aminobenzoic acid in ethanol. They were recrystallized from methanol before use. Their characteristics are shown in Table 1.

Table 1. Characteristics of Cn-BBAs employed in this work.



R	Elemental Analysis (%)			Temperature(°C) of transition to		
	C	H	N	Smetic	Menatic	Isotropic
n-C_5H_{11}	72.77	6.00	4.57	--	175	252
	(72.84)	(7.08)	(4.47)	--	(214)	(260)
n-C_6H_{13}	73.70	6.90	4.00	--	170	256
	(72.84)	(7.08)	(4.31)	(160)	(172)	(260)
n-C_8H_{17}	74.53	7.12	3.58	156*	217*	--
	(74.78)	(7.65)	(3.97)	(155)	(216)	(250)
n-$C_{10}H_{21}$	75.53	8.32	3.60	132*	230*	240*
	(75.59)	(8.13)	(3.67)	(132)	(232)	(242)

Elemental analysis: ( ) calculated values.

Temperature: * from DSC,

( ) by Patel, et al. by optical microscope[3].

Both poly-DMAMA and the benzoic acids were dissolved in alcohols(methanol, ethanol, or n-propanol), the solutions were mixed, and after filtering a small amount of insoluble matter the solvent was evaporated at room temperature in atmospheric pressure on a Teflon plate. The films were dried in vacuum at room temperature before characterization. The molar ratio of the acids to the poly-DMAMA was chosen to be 0.8.

CHARACTERIZATION

A polarized optical microscope, Olympus BHC fitted with a Leitz heating plate, was used for microscopic observation. X-ray diffractometry was performed by using a Siemens D-500 diffractometer with Cu Kα radiation of 1.5406 Å. A DuPont differential scanning calorimeter, Model 910, was used for thermal analysis. IR spectra were taken using a Nicolet 510p FT-IR Spectrometer equipped with an optical microscope, Model, Nic-Plan, filtted with a hot stage.

RESULTS AND DISCUSSION

The thermal analysis results of the benzoic acids-poly-DMAMA systems are shown in Fig. 1. It can be seen that all of the acids, except p-ethoxybenzoic acid, show an endotherm at around 110 °C, which is attributed to the separation of the acids from poly-DMAMA. In the case of benzoic acid, sublimation was observed. The enthalpy of dissociation increased with increase in the acidity of the benzoic acids, as shown in Table 2. It should be borne in mind however, that not all of the acids are forming salts, and some exist as free acids in the polymer. Nevertheless, it can be said that the salts dissociate at 105 - 115 °C. The anomalous behavior of p-ethoxybenzoic acid, which showed an exotherm instead of an endotherm, cannot be explained at present, but it was found in the course of this work that p-ethoxybenzoic acid does not form a salt with the amino group of the polymer. The mixture forms a nematic mesophase at 110 -120 °C which is being investigated and will be reported in the future.

Cn-BBAs are known to form liquid crystalline phase. These have been studied by Patel et al.[3] using an optical microscope, as shown in Table 1. The results of thermal analysis of C10-BBAs are shown in Figs. 2 and 3, respectively. It can be seen from the figure that all of the acids show an endotherm prior to melting, which is attributed to a rearrangement of crystalline structure, although what type of phase change is taking place is unknown. In fact, the IR spectra of these acids at room temperature did not show any peak at around 3,400 cm^{-1} for the carboxylic proton, and the carbonyl peaks were in the range of 1683-1690 cm^{-1}, indicating that these acids exist as dimers. IR spectra of C8-BBA were taken at 120, 150 and 180 °C, but no dissociation to the monomeric acid was observed. Patel[3] reported that the liquid crystalline phase of Cn-BBAs is of the dimer.

Table 2. Observed endothermic enthalpy(ΔH) of the dissociation of benzoic acids from poly-DMAMA.

p-Substituents.	n-BuO-	EtO-	MeO-	HO-	N≡C-	O_2N-
ΔH(cal/g)	0.35	+0.28	1.78	1.46	3.78	3.05

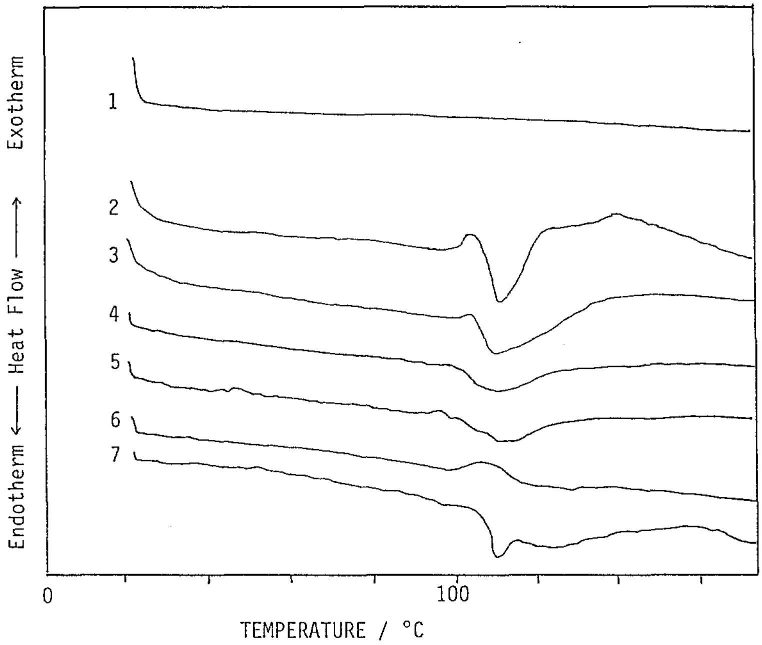


Fig. 1. DSC Curves of poly-DMAMA/benzoic acid (BA) systems.
1 : Poly-DMAMA alone, 2 : with p-C≡N-BA, 3 : with p-NO_2-BA,
4 : with p-HO-BA, 5 : with p-CH_3-BA, 6 : with p-C_2H_5O-BA,
7 : with p-C_4H_7-BA.

The DSC curves of the mixed systems are also shown in Figs. 2 and 3. It can be seen that the thermal behaviors of the acids do not change appreciably on mixung with the polymer, suggesting that the systems mainly consist of simple mixtures without forming salts. The X-ray diffraction patterns of the acids alone and the acids in the amorphous poly-DMAMA were found to be almost identical, and the IR absorption band of the carbonyl groups of the acids alone and in the polymer were also the same. These observations indicate that there is no appreciable interaction between the acids and the polymer, and it seems that the majority of the acids remain as the dimer rather than in the form of salts with the tertiary amino groups of the poly-DMAMA.

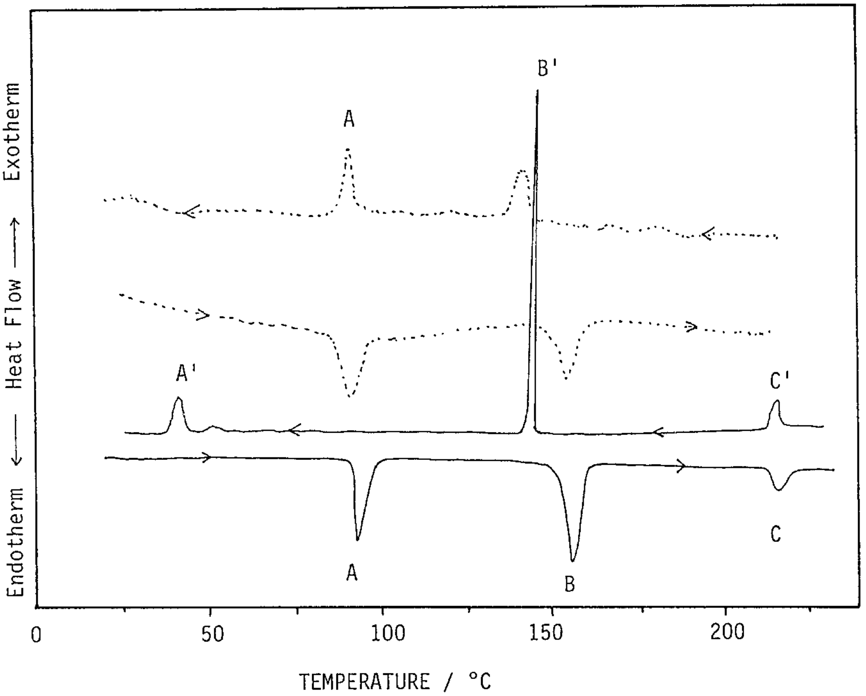


Fig. 2. DSC Curves of C8-BBA(———) and of poly-DMAMA/C8-BBA mixed system(·······). → : Heating. ← : Cooling.
A, A' : Phase change(Rearrangement of C8-BBA crystal structure). B : Melting, B' : Solidification. C, C': Isotropic point.

The optical microscopic observation of the mixed systems showed that the system become fluid at temperatures somewhat below the melting point of the acids; C5-BBA/poly-DMAMA (160 °C), C6-BBA/poly-DMAMA (155 °C), C8-BBA/poly-DMAMA (140 °C) and C10-BBA/poly-DMAMA (125 °). poly-DMAMA melts above 200 °C, and therefore the acids seem to be acting as plasticizers. At these temperatures, where the systems become viscous liquids, the acids probably exist as dimeric acids, not in the form of salts, judging from their IR spectra taken at elevated temperature. Therefore, these acids are considered to have good miscibilities with poly-DMAMA not because of an acid-base reaction but by other interactions such as the dipole-dipole interaction through the carbonyl groups, and Van der Waals interactions between the aliphatic parts of the acid and the polymer.

The thermal behaviors of the mixtures above the melting temperatures are not consistent. In the case of the C10-BBA/poly-DMAMA system for example, some unmelted crystals of C10-BBA are floating in the liquid at 120-130 °C and they melt slowly with an increase in the temperature. At around 140 °C some liquid crystal particles are formed in the melt, and about 215 °C the system becomes totally iso-

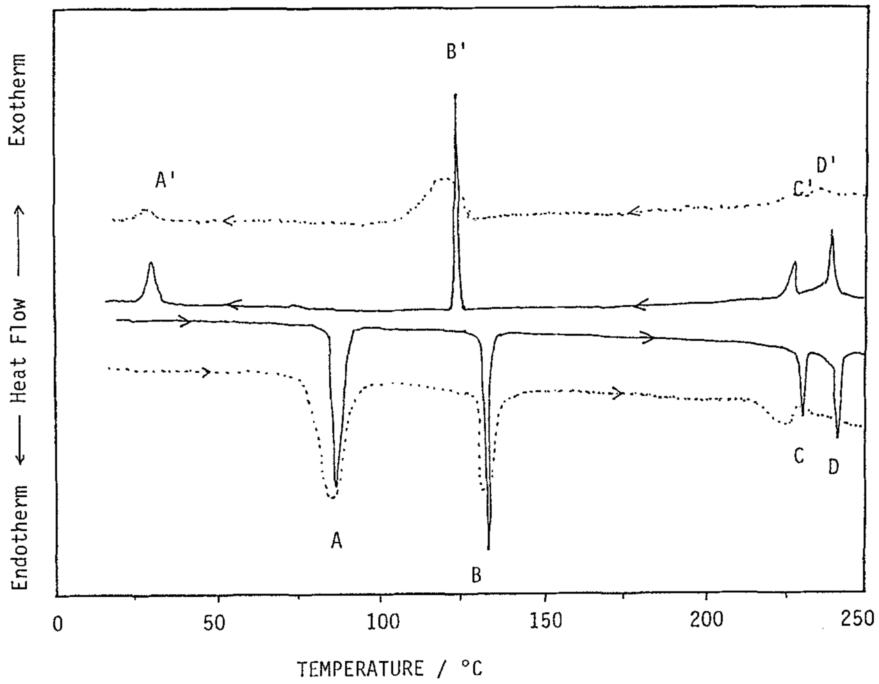


Fig. 3. DSC Curves of C10-BBA(——) and of poly-DMAMA/C10-BBA mixed sytem(·······). → Heating. ← : Cooling.
A, A' : Phase change(Rearrangement of C10-BBA crystal structure). B, B' : Melting and solidifying. C: Nematic.
D,D':Isotropic point.

tropic. On cooling from 220 °C, numerous micro worm-like liquid crystals start to appear dancing in the melt at around 200 °C, but they rapidly become round particles of liquid crystals, which collide with each other and form larger particles with a Schlieren structure. Finally they solidify at about 110 °C. Similar behaviors are observed for C8-BBA, but for C6 and C5-BBAs very few liquid crystal particles were observed. The numbers of liquid crystalline particles which appear on cooling for the C8 and C10-BBA/poly-DMAMA systems are not consistent; sometimes many and sometimes few LC particles appear.

In order to see the effect of heating on the morphology of the mixed systems, the samples were preheated for 30 minutes at the melting temperatures of the corresponding Cn-BBAs. The thermal behavior of the acid which was observed before the heat treatment(Fig. 3), completely disappeared, and the system became totally amorphous. No liquid crystal was observed under the optical microscope. The peaks corresponding to the crystal structure of C10-BBA also disappeared, giving an totally amorphous material, as shown in Fig. 4 . The same phenomena were observed for other BBAs.

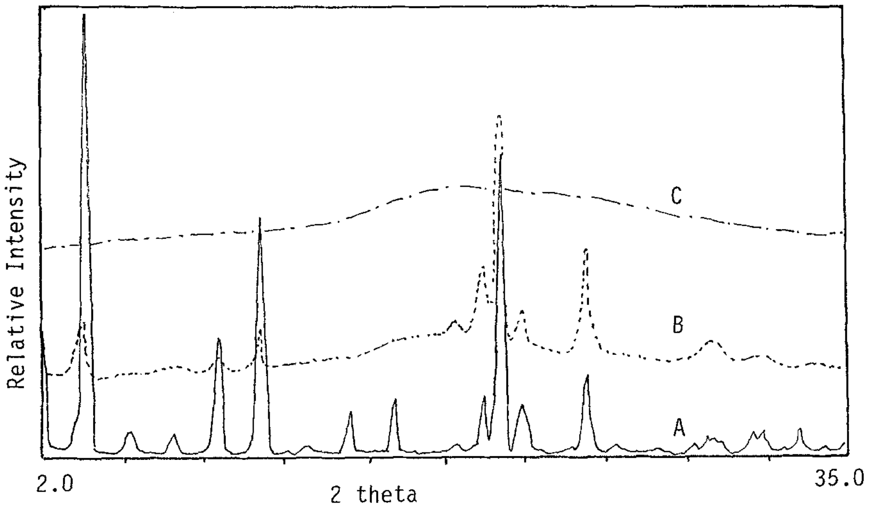


Fig. 4. X-Ray Diffraction patterns of C10-BBA(A), Poly-DMAMA/C10-BBA mixture(B) and the mixture treated at 140°C for 30 minutes(C).

It can be concluded that Cn-BBAs does not form monomeric acids on heating and exist as dimers both alone and in poly-DMAMA. They seem to remain unchanged upon contact with the tertiary amine groups of the polymer, probably the acidities of these Cn-BBAs are very low, compared with those of the simple benzoic acids. Although they form liquid crystalline particles in poly-DMAMA, repeated heating decreases the number of particles, and eventually totally homogeneous mixtures are obtained, due to the good miscibility with the host polymer.

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