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Synthesis and Physical Properties of Blends of Donor Polymers from 2-(*p*-Dimethylaminobenzyl)-1,3-propanediol and Acceptor Polymers from 2-(3,5-Dinitrobenzyl)-1,3-propanediol: A New Phase Composed of Donor and Acceptor Polymers

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ABSTRACT: Donor (or acceptor) poly(carbonate)s or poly(phthalate)s were prepared from 2-(*p*-dimethylaminobenzyl)-1,3-propanediol (or from 2-(3,5-dinitrobenzyl)-1,3-propanediol). The spectral, thermal, mechanical, and optical properties were measured for the donor polymers, the acceptor polymers, and their blends in order to clarify the effects of the formed electron-donor-acceptor (EDA) complexes. The donor and acceptor polymer blends were found to consist of two-phase structures by differential scanning calorimetry, torsional braid analysis, and scanning electron microscopy. It was noticed that the tensile modulus of the polymer blends was larger than that of each component polymer. The increased mechanical strength was interpreted in terms of the EDA interaction on the boundaries between globules and surroundings.

KEY WORDS 2-(*p*-Dimethylaminobenzyl)-1,3-propanediol / 2-(3,5-Dinitrobenzyl)-1,3-propanediol / Electron-Donor-Acceptor Complex / Donor Polymer / Acceptor Polymer / DSC / TBA / Tensile Modulus / Phase-Separation / Scanning Electron Microscopy /

It is well known that the mechanical properties of polymers are much affected by binding forces, such as dispersion force, hydrogen bond, dipole–dipole interaction due to the formation of electron-donor-acceptor (EDA) complexes, etc. There have been a few studies on the effects of intermolecular interaction due to the formation of EDA complexes on structure and mechanical properties of polymers.

Hallensleven and Kuppel found that the viscosity of poly(4-vinylpyridine) in solution is strongly influenced by added tetracyanoethylene (TCNE).[1] Boudevska *et al.* observed the structure formation of complexes of poly(phenyl methacrylate), poly(2-naphthyl methacrylate), and poly(vinylcarbazole) with TCNE, using electron microscopy and X-ray diffraction.[2] Ohshima *et al.* demonstrated that the modulus of the complex of poly[4-(*m*-dimethyl aminophenoxy)butylacrylate] with *p*-chloranil within a high temperature range increases as a result of the formation of physical crosslinking due to the formed EDA complexes in the polymer matrix.[3] Sulzberg and Cotter prepared the acceptor polymers having nitrophthalate units in main chain and the donor polymers from aryliminodiethanols where the aryl was phenyl or *p*-anisyl, and studied the effects of blending on glass transition temperature, tensile modulus, solution viscosity, etc.[4] This is the first report on the EDA complexes formed by blending donor polymers and acceptor polymers.

We have been interested in the blends of donor polymers and acceptor polymers, since certain properties of these complexes may, in future, have promise not only from a mechanical, but also from photoreactive, photoconductive, electrical properties, etc. points of view. Sulzberg *et al.* used the polymers containing the donor or the acceptor residues in the main chain. We used the polymers possessing pendent-type donor or acceptor groups to strengthen the EDA interaction between the donor and acceptor polymers by decreasing restriction of main chain. Moreover, the structures of donor and acceptor monomers are designed to provide a better compatibility with blends in this study.

We prepared 2-(*p*-dimethylaminobenzyl)-1,3-

propanediol as the donor monomer and 2-(3,5-dinitrobenzyl)-1,3-propanediol as the acceptor monomer; these monomers were then reacted with iso- or terephthaloyl chloride or diphenyl carbonate to yield the corresponding poly(iso- or terephthalate)s or poly(carbonate)s. The donor and acceptor blends were studied in view of intermolecular interaction due to the formation of EDA complexes. The physical properties and structures of these polymers by means of visible spectroscopy, differential scanning calorimetry, torsional braid analysis, tension test, and scanning electron microscopy.

EXPERIMENTAL

Materials

2-(p-Nitrobenzyl)-1,3-propanediol (**2**). A mixture of 80 g (0.27 mol) of diethyl 2-(*p*-nitrobenzyl)malonate (**1**),[5] 60.4 g (0.54 mol) of calcium chloride, 41.2 g (1.08 mol) of sodium borohydride, and 800 ml of dry THF were stirred for 10 h at room temperature, then cooled over an ice bath. To the cooled solution was added 100 ml of water dropwise, and then an additional 500 ml of water. The resulting mixture was acidified by adding 100 ml of concd hydrochloric acid. After removal of THF from the separated upper layer, the residue was extracted with ether, and dried. By removal of the ether, the obtained crude product was recrystallized from benzene to yield 40.2 g (70.3%) of **2**: mp 65.5—66.5°C; IR (KBr) 3260, 1620, 1550, 1360, and 1035 cm^{-1}; NMR ($CDCl_3$) δ 8.13 (d, 2H, aromatic), 7.35 (d, 2H, aromatic), 3.62—3.74 (m, 4H, CH_2–O), 2.80 (d, 2H, Ph–CH_2), 2.72 (s, 2H, OH), and 2.05 ppm (m, 1H, CH). *Anal.* Calcd for $C_{10}H_{13}NO_4$: C, 56.86%; H, 6.20%; N, 6.63%. Found: C, 56.76%; H, 6.41%; N, 6.70%.

2-(p-Dimethylaminobenzyl)-1,3-propanediol (**3**). To a solution of 10 g (0.047 mol) of **2** in 50 ml of ethanol was added 9.2 ml of 40% formaldehyde solution and 0.5 g of 10% palladium on charcoal, and the mixture was hydrogenated with a Parr hydrogenation apparatus[6,7] filled with hydrogen at a pressure of about 4 kg cm^{-2} at room temperature until the pressure ceased to drop, and was then filtered. Following removal of the ethanol and formaldehyde, the residue was recrystallized from a mixed solvent of benzene and ligroin (1 : 1 v/v). The yield of **3**, at mp 94—95°C (reported[8] mp 95—96°C), was 8.6 g (86.8%): IR (KBr) 3360, 2800, 1620, 1535, 1360, 1240, 1040, and 1020 cm^{-1}; NMR ($CDCl_3$) δ 7.02 (d, 2H, aromatic), 6.64 (d, 2H, aromatic), 3.58—3.70 (m, 4H, CH_2–O), 2.94 (s, 2H, OH), 2.88 (s, 6H, CH_3), 2.49 (d, 2H, Ph–CH_2), and 2.00 ppm (m, 1H, CH); high-resolution mass spectrum, *m/e*: Calcd for $C_{12}H_{19}NO_2$, 209.1414; Found, 209.1361; *Anal.* Calcd for $C_{12}H_{19}NO_2$: C, 68.86%; H, 9.15%; N, 6.69%. Found: C, 68.64%; H, 8.88%; N, 6.68%.

2-(3,5-Dinitrobenzyl)malonic acid (**5**). A mixture of 40 g (0.118 mol) of diethyl 2-(3,5-dinitrobenzyl)malonate (**4**)[5] and 800 ml of concd hydrochloric acid was heated at 70°C for 1 h, cooled, and then filtered. The filtrate was extracted with ether. The extract was washed with a 10% aqueous sodium carbonate solution and water, and then dried. After evaporating the ether, the crude product was recrystallized from a mixed solvent of benzene and methanol (30 : 1 v/v). The yield of **5** melting at 131.5—133°C was 21 g (62.9%): IR (KBr) 3400, 1735, 1600, 1545, and 1350 cm^{-1}; NMR [$(CD_3)_2CO$] δ 9.68 (s, 2H, COOH), 8.84 (t, 1H, aromatic), 8.66 (d, 2H, aromatic), 3.87—4.22 (m, 1H, CH), and 3.50 ppm (d, 2H, CH_2). *Anal.* Calcd for $C_{10}H_8N_2O_8$; C, 42.26%; H, 2.84%; N, 9.86%. Found: C, 42.35%; H, 2.83%; N, 9.63%.

2-(3,5-Dinitrobenzyl)-1,3-propanediol (**6**). To 280 ml of 0.97 mol l^{-1} diborane–THF solution was added dropwise a solution of 13 g (0.0458 mol) of **5** in 50 ml of THF. The mixture was stirred for 9 h at room temperature and then for 5 h at 50°C. After cooling, water was added dropwise with care to the mixture until there was no longer evolution of hydrogen. After removal of THF, the residue was extracted with ether and dried. The crude product obtained was chromatographed on a column packed with activated alumina (Wako; 300 mesh, 400 × 65ID mm) in chloroform. After the by-products were eluted with chloroform, methanol was used as the eluent, and crude **6** was obtained from the eluate. After evaporation it was recrystallized from benzene to yield 7.0 g (59.7%) of **6** melting at 124—125°C: IR (KBr) 3270, 1600, 1540, 1355, and 1035 cm^{-1}; NMR [$(CD_3)_2SO$] δ 8.63 (t, 1H, aromatic), 8.44 (d, 2H, aromatic), 4.23 (s, 2H, OH), 3.30—3.39 (m, 4H, CH_2–O), 2.86 (d, 2H, Ph–CH_2), and 1.90 ppm (m, 1H, CH). *Anal.* Calcd for $C_{10}H_{12}N_2O_6$: C, 46.88%; H, 4.72%; N, 10.93%. Found: C, 47.01%; H, 4.79%; N, 10.98%.

Other materials. Diphenyl carbonate, isophthaloyl chloride, and terephthaloyl chloride obtained commercially were purified by distillation under reduced pressure. Pyridine and 1,2-dichloroethane were purified conventionally.

Polymerization

Poly(carbonate). Donor polymers or acceptor polymers were synthesized according to the modified procedure of the literature.[9]

Donor polymers: A mixture of 0.500 g (2.39 m mol) of the donor monomer (**3**) and 0.512 g (2.39 m mol) of diphenyl carbonate was heated at 140—150°C with stirring for 6 h under a pressure of 10—20 mmHg, and then evacuated to 0.3 mmHg at the same temperature for 4 h. The by-product, phenol, was continuously removed from the reaction system. The reaction product was reprecipitated from a benzene–methanol system and dried at 60°C *in vacuo*. The yield was 0.38 g (65%). The acceptor polymer was synthesized similarly from the acceptor monomer (**6**) and reprecipitated from acetone–methanol system; yield, 75%.

Poly(iso- or terephthalate). Polyphthalates were made from the donor monomer (**3**) (or the acceptor monomer (**6**)) and isophthaloyl chloride or terephthaloyl chloride according to the Sulzberg's method;[4] yield, 60—66%.

Blends of Donor Polymers and Acceptor Polymers

The repeating units of the synthesized donor and acceptor polymers are shown in Figure 1. Three kinds of the blends of donor polymers and acceptor polymers (donor : acceptor = 1 : 1) were prepared by mixing their THF solutions and by drying the mixture completely at 60°C *in vacuo* for 2 days. The symbols are the same as those shown in Figure 1:

$$1_{CT}=1_d+1_a,\ 2.1_{CT}=2.1_d+2.1_a,$$
$$2.2_{CT}=2.2_d+2.2_a$$

Absorption Maxima

The visible spectra of the polymers in THF were measured with a Union Giken High-Sensitive Spectrophotometer SM-401 at room temperature. The wave length of the absorption maxima (λ_{max}) of the blends was measured by placing a THF solution of the same concentration of the acceptor polymer as a reference, since the tail of its absorption overlapped with the absorption maximum of EDA complexes.

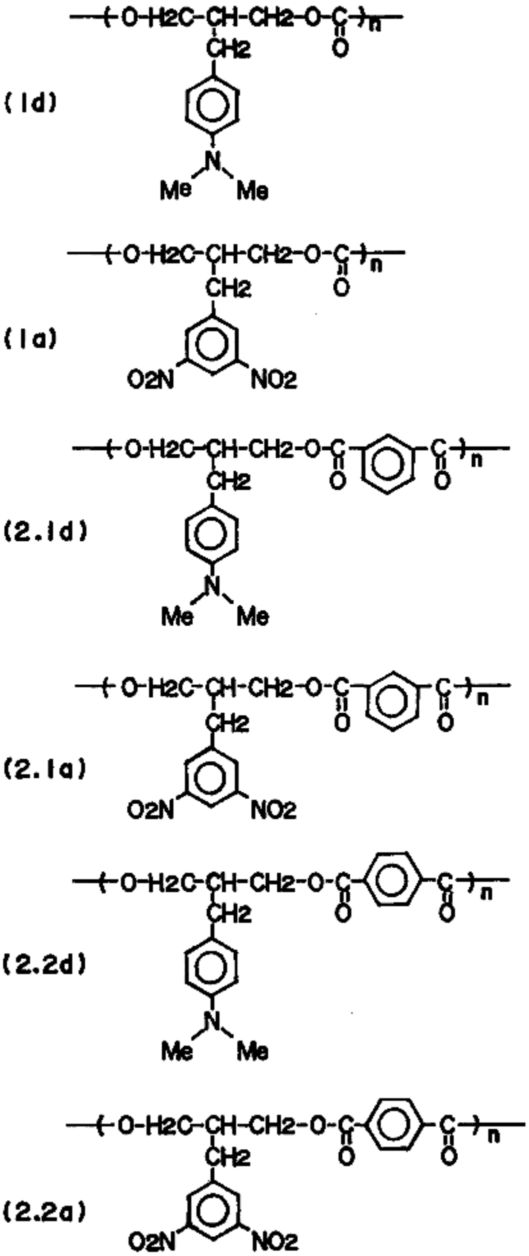


Figure 1. Used donor polymers and acceptor polymers.

Differential Scanning Calorimetry (DSC)

DSC thermograms were carried out over a temperature range from 240 to 420 K at a heating rate of 20 K min^{-1} with a Perkin-Elmer DSC-2. The glass transition temperature (T_g) was determined as that temperature at which an endothermic peak is intermediate between those in a glassy and rubbery region. The calorimetric differences between, before, and after T_g defined by Wunderlich (ΔC_p)[10] were obtained from the observed DSC thermograms.

Torsional Braid Analysis (TBA)

Dynamic thermomechanical spectra (at about 1.1 Hz) were obtained over a temperature range of 10 to 190°C at a heating rate of 0.8°C min^{-1} by means of a torsional vibration analyzer (Model RD-10, Rhesca Co., Ltd.). Test specimens were prepared as follows: a glass fiber braid was immersed in a THF solution of a polymer and then dried at 80 – 120°C *in vacuo* for 2 days.

Tension test

This test was carried out at a strain rate of 1 mm min^{-1} at room temperature with a tension tensile tester (Tensilon, Model UTM-2, Toyo Baldwin Co., Ltd.). Test specimens were prepared by compression molding at 120°C *in vacuo* with a vacuum press (Model SS-VP-50, Sibayama Scientific Co., Ltd.).

Electron Microscopy

The fracture surface of polymer films made by compression molding was treated by an ion-etching method with anion coater (Eiko Engineering Co., Ltd., Model IB-2, working conditions: AV-700 V, 5—7 mA, 3 h, *in vacuo*), and coated with gold *in vacuo*. Observation was carried out with a scanning electron microscopy (Hitachi-Akashi-MSM-4 Type).

Molecular Weight Measurement

The number average molecular weight of the polymers was determined using a Toyo soda gel permeation chromatograph (GPC) (solvent, THF) [TSK-GEL G 2000 H (60 × 0.75 ID cm) + TSK-GEL G 4000 H (60 × 0.75 ID cm)] and the ratio of the weight average molecular weight to the number average (M_w/M_n) was calculated from the obtained GPC curves using standard polystyrenes (see Table I).

Table I. Number-average molecular weights (M_n), molecular weight distributions (M_w/M_n), and absorption maxima (λ_{max}) of donor and acceptor polymers

Polymer	M_n	M_w/M_n	λ_{max}[b]/nm
1_d	6100	4.21	270, 304
1_a	5700	2.75	272, 300^{sh},[a] 312^{sh}
2.1_d	2800	4.29	268, 288, 304
2.1_a	2900	2.34	268, 288^{sh}, 312^{sh}
2.2_d	4600	2.59	268, 292, 308^{sh}
2.2_a	4000	5.90	269, 292^{sh}, 312^{sh}

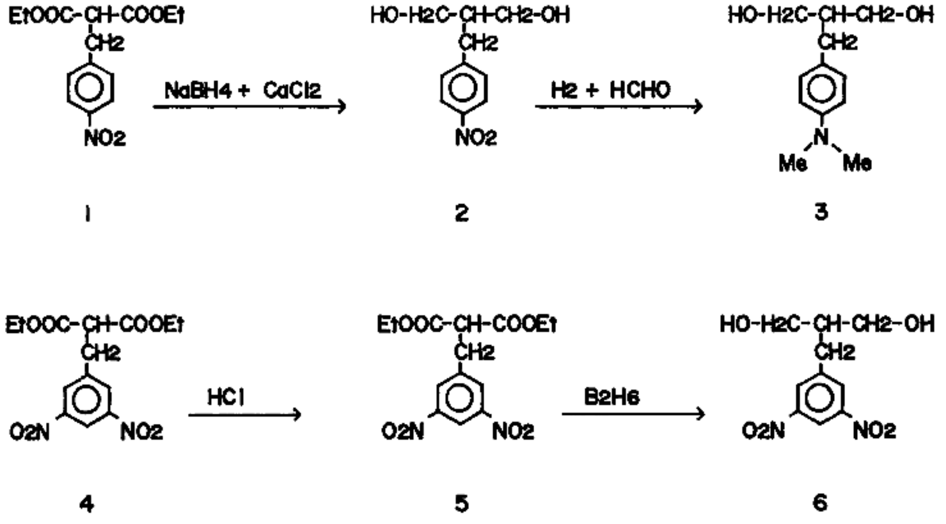
[a] sh, shoulder.

[b] Solvent, THF.

RESULTS AND DISCUSSION

Synthesis

2-(*p*-dimethylaminobenzyl)-1,3-propanediol (**3**) was readily obtained by the reductive alkyl-



Scheme 1.

ation of 2-(*p*-nitrobenzyl)-1,3-propanediol (**2**), prepared by the reduction of diethyl 2-(*p*-nitrobenzyl)malonate with sodium borohydride and calcium chloride. Diethyl 2-(3,5-dinitrobenzyl-)malonate (**4**) could not be ordinarily converted into 2-(3,5-dinitrobenzyl)-1,3-propanediol (**6**) by alkaline reducing agents, because **4** is very unstable in alkaline media owing to the presence of two nitro groups having strong electron-accepting capacities. Therefore 2-(3,5-dinitrobenzyl)malonic acid obtained by the hydrolysis of **4** was reduced to **6** with diborane.

Spectra of EDA Complexes

The formation of EDA complexes was easily recognized by appearance of the red color on blending the donor and the acceptor polymers, both of which are colorless or pale yellow. By optical microscopic observation, it was found that the red color of every blend disappeared at the softening temperature, for instance, 100—115°C for 1_{CT} and returned when the blend was cooled. Therefore it is clear that the formation reaction of such EDA complexes is reversible, and the formed complexes are thermally stable without decomposition under the experimental conditions. The obtained absorption maxima in the blends are shown in Table II.

Table II. Absorption maxima of blends of donor and acceptor polymers

Blend	Color	λ_{max}/nm[a,b]
1_{CT}	red	436
2.1_{CT}	red	442
2.2_{CT}	red	—[c]

[a] Solvent, THF.

[b] Spectra were determined by placing an acceptor solution in the reference beam.

[c] Spectra could not be determined owing to difficulties in solubilizing the sample.

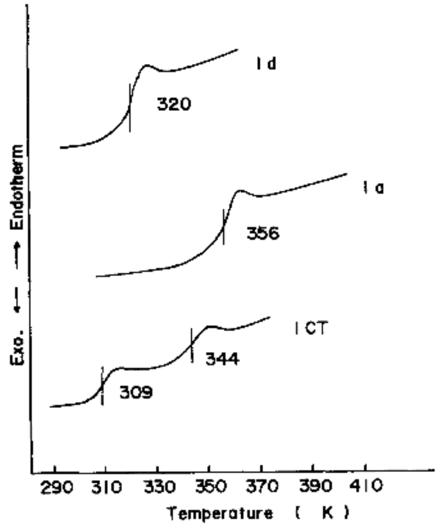


Figure 2. DSC thermograms of 1_d, 1_a, and 1_{CT}.

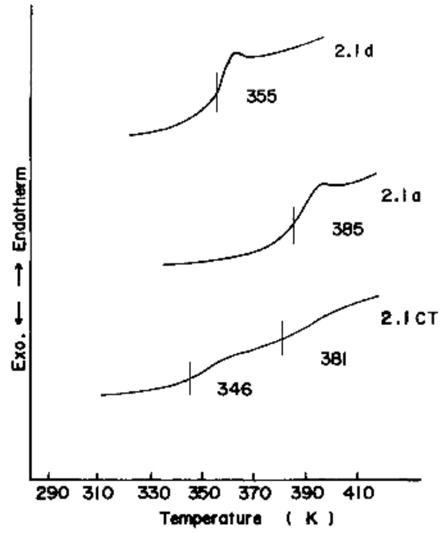


Figure 3. DSC thermograms of 2.1_d, 2.1_a, and 2.1_{CT}.

Differential Scanning Calorimetry (DSC)

The obtained DSC thermograms are shown in Figures 2, 3, and 4. Some characteristic parameters obtained therefrom are summarized in Table III. From these data, it is obvious that both the two T_g's observed in the blends and ΔC_p at the respective T_g correspond to those of each component of the blends, meaning that the blends almost consist of the phase-separated structures as a result of the weakness of the intermolecular interaction of the formed EDA complexes.

When three kinds of blends were compared with each other, it was found that with 1_{CT}, the two T_g's are clearly separated, but it was difficult for those with 2.1_{CT} and 2.2_{CT} to be separated completely. This may show that 2.1_{CT} and 2.2_{CT} have a better compatibility than does 1_{CT}.

The difference among 1_{CT}, 2.1_{CT}, and 2.2_{CT} in the DSC thermograms may be caused by the following

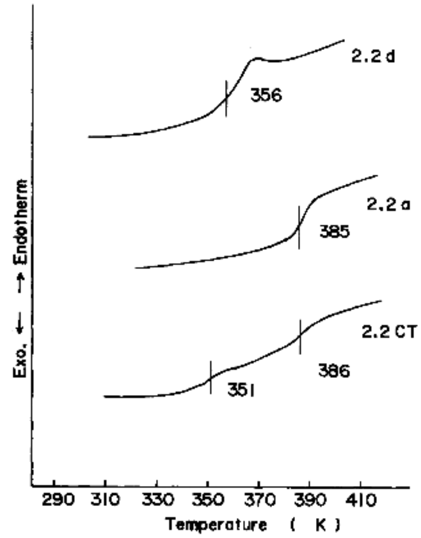


Figure 4. DSC thermograms of 2.2_d, 2.2_a, and 2.2_{CT}.

Table III. Glass transition temperature[a] and ΔC_p[b] of donor and acceptor polymers, and blends obtained from DSC thermograms

		Polymer			
		Donor	Acceptor	Blend	
1	T_g	46.7	83.4	35.5	71.0
	ΔC_p	10.85	9.74	4.25	5.29
2.1	T_g	81.9	111.9	73.0	108.0
	ΔC_p	9.83	9.49	4.42	4.98
2.2	T_g	83.1	112.0	77.8	113.0
	ΔC_p	9.77	9.17	6.39	5.31

[a] T_g/°C.

[b] Calorimetric difference before and after T_g, defined by Wunderlich,[10] $\times 10^2$/cal g^{-1}.

differences: (1) chemical structures; (2) molecular weights of the donor and the acceptor polymers; (3) strength of intermolecular interaction due to the formation of EDA complexes, etc.

Although Sulzberg *et al.* reported only one T_g for three kinds of blends,[4] two T_g's were observed in our three blends. this inconsistency may be attributed to some of the following differences: (1) the structure of the polymers used (all polymers contain the donor- or the acceptor-units in the main chain, whereas our polymers in the side chain), and (2) the strength of intermolecular interaction is due to the formation of the EDA complexes, that is, their acceptor polymers consist of a mononitroisophthaloyl group (the values of λ_{max} of the EDA complexes which are inversely proportional to the energies of the EDA complex formations; 391—398 nm), whereas our acceptor polymers consist of 3,5-dinitrobenzyl group, (λ_{max} of the EDA complexes; 436—442 nm).

Torsional Braid Analysis (TBA)

The results of the TBA measurements are shown in Figures 5, 6, 7, and 8. As seen in the DSC thermograms, the clearly separated two T_g's in the blends, corresponding to the T_g of each component of the blends, were found in this case, too, although

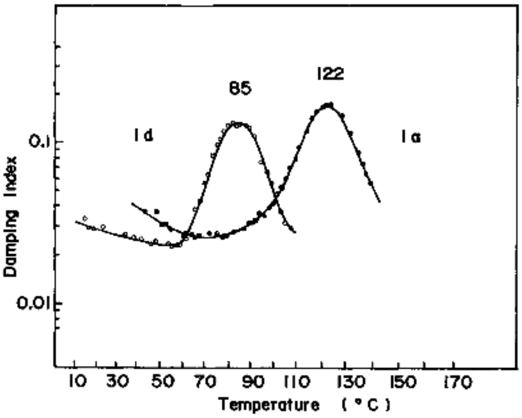


Figure 5. Relationship between damping index and temperature of 1_d and 1_a.

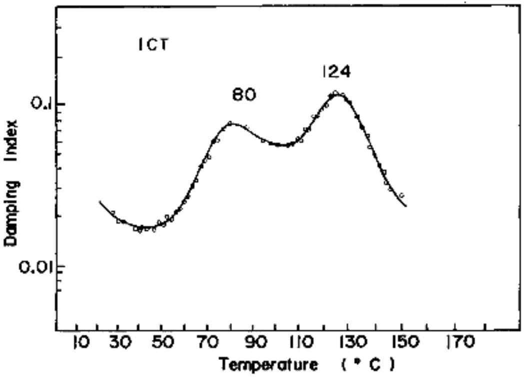


Figure 6. Relationship between damping index and temperature of 1_{CT}.

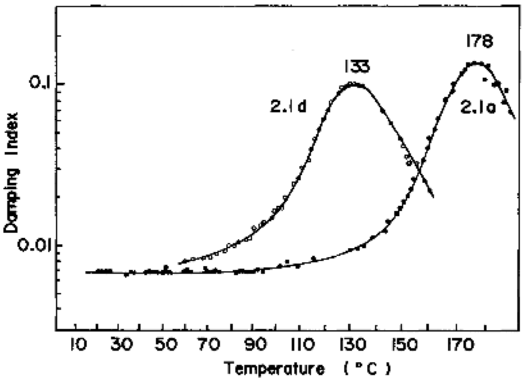


Figure 7. Relationship between damping index and temperature of 2.1_d and 2.1_a.

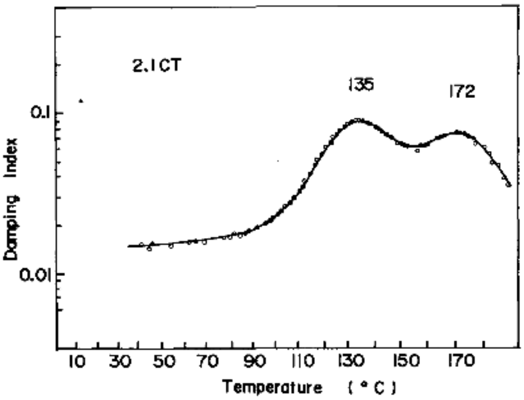


Figure 8. Relationship between damping index and temperature of 2.1_{CT}.

the values of the T_g's observed by TBA are higher than those by DSC.

Tension Test

A tension test was carried out on 2.1_d, 2.1_a, and 2.1_{CT}. The results obtained are summarized in Table IV. It was found that there is little difference between these three kinds of polymers in regard to the values of ultimate elongation, but the values of the yield stress and tensile modulus of the blend are relatively higher than those of the component polymers.

Sulzberg *et al.* also reported that the tensile modulus of the blends of the donor polymers and the acceptor polymers is larger than that of each component of the polymers: the tensile modulus of poly[oxycarbonyloxyethylene-(*p*-methoxyphenyl)-iminoethyleneoxycarbonyloxy-4,4′-isopropylidene-1,1′-diphenylene] and poly(oxycarbonyloxyethyleneoxy-5-nitroisophthaloyloxyethyleneoxycarbonyloxy-4,4′-isopropylidene-1,1′-diphenylene) are 335,000 and 260,000 psi, respectively, but that of their blend (1 : 1) is 360,000 psi.[4]

Table IV. Ultimate elongation, yield stress, and tensile modulus of 2.1_d, 2.1_a, and 2.1_{CT}

Property	2.1_d	2.1_a	2.1_{CT}
Ultimate elongation/%	1.17	1.16	1.20
Yield stress/kg cm^{-2}	69.3	64.4	82.8
Tensile modulus/kg cm^{-2}	68.7	61.9	73.5

Moreover, in case of ionomers, Dieterich *et al.* reported that such physical properties as tensile strength and modulus are more stronger than those of the EDA complexes described above.[11]

In our study, it should be noticed that several mechanical properties of the blend were strengthened to some extent, though the blend consisted of the phase-separated structure.

Electron Microscopy

Electron microscopic observations of the structure formation of polymeric EDA complexes were reported by Boudevska *et al.*[2] According to their report, the dendrit-like supermolecular structures were found in the complexes casted from chloroform solutions of poly(phenyl methacrylate), poly(2-naphthyl methacrylate), or poly(vinylcarbazole) with TCNE.

The fracture surfaces of the films made by a compression molding of 2.1_d, 2.1_a, or 2.1_{CT} were observed with a scanning electron microscope. No structure, unlike that in Boudevska's report, could not be discerned in the blend.

We applied ion-etching treatment to the above-

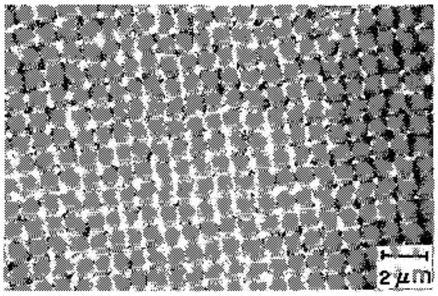


Figure 9. Scanning electron micrograph of sample 2.1_{CT} to which ion-etching treatment was applied.

mentioned samples to clarify the structure in the blend. The observed result is shown in Figure 9; that is, the globular structures were clearly observed in the blend. This may be accounted for by considering that the boundary between the two separated phases clearly appeared as a result of the destruction of any one of the two components by the ions.

From these results, it was found that the blend consists almost completely of the two phases, and such mechanical properties as tensile modulus are made better in spite of the weak interaction between two phases on the boundaries.

CONCLUSIONS

Donor polymers from 2-(*p*-dimethylaminobenzyl)-1,3-propanediol, acceptor polymers from 2-(3,5-dinitrobenzyl)-1,3-propanediol, and blends of these were made. From the DSC and TBA measurements, the blends were found to consist of two separated phases. However, the mechanical properties of each blend such as yield stress and tensile modulus were somewhat improved upon as a result of the formation of EDA complexes. An electron microscopic observation showed two phase structures of the blend and the reinforced mechanical properties of the blend were assumed to arise from the increased interaction due to the EDA complex formations on the boundaries of the two phases.

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