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Miscible Blends from Poly(2,6-dimethyl-1,4-phenylene oxide) and Poly(epichlorohydrin) Containing Pendant Electron-Donor and Electron-Acceptor Groups[†]

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ABSTRACT: The structures of nonmiscible poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and poly(epichlorohydrin) (PECH) were modified by introducing either donor (carbazolyl) or acceptor (3,5-dinitrobenzoyl) pendant units connected to the polymer chains through methylene spacer groups. A phase-transfer-catalyzed esterification of bromobenzyl or chloromethyl groups with the potassium salts of *N*-carbazolylacetate, *N*-carbazolylpropionate, and 3,5-dinitrobenzoate groups was used to modify the structure of both PPO and PECH. The phase-transfer-catalyzed alkylation of carbazole with the chloromethyl groups of PECH was also used to synthesize a PECH containing pendant *N*-carbazolyl groups. Polymer mixtures of donor-containing PECH and acceptor-containing PPO were analyzed by differential scanning calorimetry and were found to become miscible when the two backbones contain donor and acceptor groups in at least 25% of the structural units. The miscibility decreased as the number of methylene spacer groups connecting the donor or acceptor to the polymer backbone increased. The glass transition temperature's composition dependence for miscible systems was analyzed by five equations available in the literature, with Kwei's equation giving the best fit in all cases.

Introduction

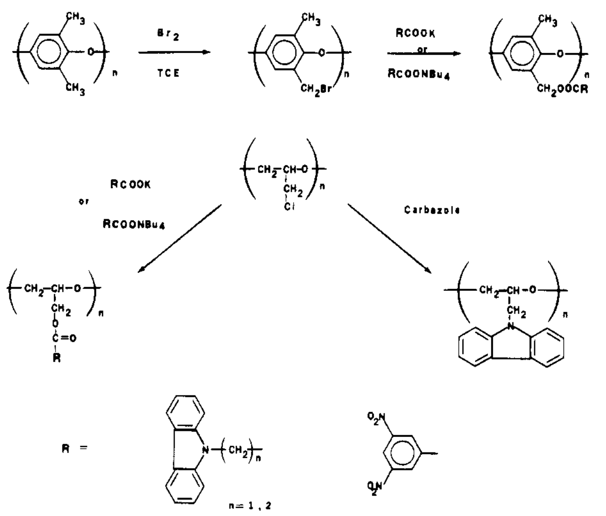
In a previous paper from our laboratory[1] we presented a study of the interchain electron donor–acceptor (EDA) complexes of several series of homopolymers containing pendant electron-donor groups with homopolymers containing pendant electron-acceptor groups. This topic has been[2–5] and still is[6–9] pursued by several other laboratories. It has already been demonstrated that strong enough interactions to induce polymer miscibility can be provided by carbazolyl groups as donors and 3,5-dinitrobenzoyl groups as acceptors, both of which are attached to the polymer backbones through methylene spacers. This is the case for homopolymers containing both donor and acceptor groups required to induce miscibility in a pair of nonmiscible polymers.

We are currently using interchain donor–acceptor interactions to prepare miscible, mesomorphic polymer blends starting from thermotropic side-chain liquid crystalline polymers and nonmesomorphic polymers.[10] One of the major reasons for this investigation is that the strategy of interchain EDA complexes for creating mesomorphic miscible blends is apparently one of the few available avenues in attaining such blends. With this goal in mind, it is essential to understand the range of concentrations of donor and acceptor groups required to create a miscible polymer system.

For this purpose we have selected two polymer backbones that are nonmiscible: a thermoplastic, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), and an elastomer, poly(epichlorohydrin) (PECH). Both polymers have polyether structures that provide basic or donor type character and consequently are not miscible. To make these polymers interact with each other, we have modified the structure of both polymer backbones by introducing either donor (carbazolyl) or acceptor (3,5-dinitrobenzoyl) type units.

The synthetic procedure used for the chemical modification of PPO involved in the first step the radical bromination of PPO methyl groups to provide a polymer containing bromobenzyl groups. The bromobenzyl groups were then esterified under phase-transfer-catalyzed reaction conditions with potassium *N*-carbazolylacetate, potassium *N*-carbazolylpropionate, and potassium 3,5-dinitrobenzoate. The two-phase reaction system involved a toluene solution of bromobenzylated PPO, solid potassium carboxylate salt, and tetrabutylammonium hydrogen sulfate (TBAH) as the phase-transfer catalyst. The same reactions were performed with the tetrabutylammonium salts of the above-presented carboxylic acids in toluene.

Scheme I



PECH was modified under similar reaction conditions, except that dimethyl sulfoxide (Me_2SO) or dimethylformamide (DMF) was used as the reaction solvent. In addition, the phase-transfer-catalyzed alkylation of carbazole with the chloromethyl groups of PECH was also used to synthesize a PECH containing pendant *N*-carbazolyl groups. Esterification routes of both PPO and PECH are presented in Scheme I.

Polymer mixtures of modified PPO with modified PECH become miscible when the two backbones contain donor or acceptor groups in at least approximately 25% of the structural units.

Experimental Section

A. Materials. The starting polymers were commercial products. PECH (BFGoodrich, $\bar{M}_n = 873000$, $\bar{M}_w = 10250000$) was purified by precipitation with methanol from chloroform solution: ^1H NMR ($CHCl_3$-*d*, ppm) 3.7 (CH_2O, CH, CH_2Cl, 5 H). PPO (Aldrich, $\bar{M}_n = 19000$, $\bar{M}_w = 49000$) was purified by pre-

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cipitation with methanol from chloroform solution: ^{1}H NMR ($CHCl_3$-*d*, ppm) 2.1 (s, CH_3, 6 H), 6.3–6.7 (2 aromatic H). All solvents were reagent grade and were used as received. Reagent-grade sodium hydroxide, potassium hydroxide, potassium bicarbonate, tetrabutylammonium hydrogen sulfate (TBAH) (Aldrich), and the other reagents were used without further purification. Carbazole (Aldrich) was purified by hot filtration and successive recrystallizations from toluene and ethanol.

Blends were prepared by separate dissolution of the component polymers in chloroform, mixing the two solutions, and casting a film. The films were then dried above the glass transition temperature (T_g) in vacuo.

B. Synthesis of 2-(*N*-Carbazolyl)propionitrile. 2-(*N*-Carbazolyl)propionitrile was synthesized through the cyanoethylation of carbazole (167 g, 1.0 mol) with acrylonitrile in the presence of 4 mL of benzyltrimethylammonium hydroxide (Triton B) (40% methanol solution) as catalyst.[10,11] After recrystallization from acetone, the yield was 80% (176 g): mp 155.5 °C; IR (KBr) 2240 ($\nu_{C\equiv N}$), 744, 720 cm^{-1} (ν_{CH} aromatic); ^{1}H NMR ($(CH_3)_2CO$-*d*$_6$, ppm) 3.02 (t, CH_2CN), 4.61 (t, NCH_2), 6.9–7.6 (m, 6 aromatic H), 8.07 (d, 2 aromatic H).

C. Synthesis of 2-(*N*-Carbazolyl)propionic Acid. 2-(*N*-Carbazolyl)propionic acid was prepared through the hydrolysis of 2-(*N*-carbazolyl)propionitrile. A mixture of 14 g of 2-(*N*-carbazolyl)propionitrile (0.66 mol), 2000 mL of ethanol, 372 g of KOH, and 1000 mL of water was stirred at reflux temperature until all the reaction mass dissolved (ca. 3 h). The obtained solution was poured into ice water and acidified with HCl. The white precipitate was filtered and dried, yielding 149 g (94.4%) white product: mp 174 °C; IR (KBr), 3015 (ν_{OH}), 1692 ($\nu_{C=O}$), 742, 720 cm^{-1} (ν_H aromatic); ^{1}H NMR ($(CH_3)_2CO$-*d*$_6$, ppm) 2.87 (t, CH_2O), 4.53 (t, NCH_2), 6.9–7.5 (m, 6 aromatic H), 7.94 (d, 2 aromatic H).

D. Synthesis of Tetrabutylammonium 2-(*N*-Carbazolyl)propionate. Tetrabutylammonium 2-(*N*-carbazolyl)propionate was prepared by the addition of a solution of 2-(*N*-carbazolyl)propionic acid (4.8 g, 20 mmol) in chloroform (60 mL) to a solution of tetrabutylammonium hydrogen sulfate (6.2 g, 20 mmol) in water (60 mL) containing sodium hydroxide (2.5 g, 63 mmol). The lower organic layer was washed with dilute sodium hydroxide (1 N) and dried over Na_2SO_4. Following the removal of chloroform, water was removed by azeotropic distillation. The resulting semisolid was used without further purification: ^{1}H NMR ($CHCl_3$-*d*, ppm) 0.5–1.6 (m, $CH_2CH_2CH_3$, 28 H), 2.5–3.1 (m, NCH_2, CH_2COO, 10 H), 4.5 (t, NCH_2, 2 H), 6.9–7.5 (m, 6 aromatic H), 7.9 (d, 2 H).

E. Synthesis of *N*-Carbazolylacetic Acid. Carbazole (50 g, 0.30 mol) was transformed into its sodium salt with sodium ethoxide (21 g, 0.31 mol) in *N*-methylpyrrolidone by distilling the formed ethanol. The solution was cooled below 10 °C, ethyl chloroacetate (42 mL, 0.39 mol) was added dropwise, and the solution was stirred overnight at room temperature. This solution was poured into water, and the resulting precipitate was collected, redissolved in boiling concentrated aqueous NaOH to hydrolyze the ester group, and acidified with HCl to liberate the free acid. The product was purified by several recrystallizations from ethanol: mp 192–215 °C (lit.[13] mp 172–174 °C); ^{1}H NMR ($(CH_3)_2CO$-*d*$_6$, ppm) 5.2 (s, CH_2), 7.0–7.6 (m, 6 aromatic H), 8.1 (d, 2 aromatic H).

F. Synthesis of Potassium *N*-Carbazolylacetate, Potassium *N*-Carbazolylpropionate, and Potassium 3,5-Dinitrobenzoate. Potassium *N*-carbazolylacetate and potassium 3,5-dinitrobenzoate were prepared by reacting a 4 N methanol solution of KOH with the corresponding carboxylic acid dissolved in methanol, followed by solvent evaporation and drying. Potassium *N*-carbazolylpropionate was prepared by reacting potassium bicarbonate stoichiometrically with 2-(*N*-carbazolyl)propionic acid in aqueous methanol (1:9), followed by solvent evaporation and drying. The salts were used without further purification.

G. Radical Bromination of PPO. A solution of bromine (2.6 mL, 0.05 mol) in 1,1,2,2-tetrachloroethane (250 mL) was added dropwise to a boiling solution of PPO (24 g, 0.2 mol in 1000 mL of 1,1,2,2-tetrachloroethane) and refluxed 1.5 h. This reaction was performed according to literature procedure.[14–18] The obtained polymer was precipitated in methanol (1200 mL) and purified by reprecipitation from chloroform into methanol: ^{1}H NMR ($CHCl_3$-*d*, ppm) 2.1 (s, CH_3), 4.3 (s, CH_2Br), 6.3–6.5 (2 aromatic H). The degree of bromination determined by comparing the area of the signal at 4.3 ppm with the area of the signal at 2.1 ppm was 0.23 bromobenzyl group per PPO structural unit. A PPO sample containing 0.53 bromomethyl group per structural unit was synthesized by doubling the amount of bromine used, and a PPO sample containing 0.14 bromobenzylic group per structural unit was synthesized by halving the amount of bromine used.

H. Esterification of Brominated PPO with Potassium 3,5-Dinitrobenzoate (DNCOO–PPO), Potassium *N*-Carbazolylacetate ($CzCH_2COO$–PPO), and Tetrabutylammonium 2-(*N*-Carbazolyl)propionate ($CzCH_2CH_2COO$–PPO). The general procedure used for the esterification of PPO is presented in the following example. Brominated PPO (0.53 bromobenzyl group per structural unit) (1 g, 3.3 mmol Br) was dissolved in toluene (75 mL), and TBAH (0.11 g, 0.32 mmol) and potassium 3,5-dinitrobenzoate (0.83 g, 3.3 mmol) were added. The reaction mixture was stirred at 60 °C for 7 h and then filtered. The filtrate was poured into methanol (150 mL), and the obtained polymer was purified by redissolving in toluene, washing with water, and reprecipitating in methanol and then dried: ^{1}H NMR ($CHCl_3$-*d*, ppm) 2.1 (s, CH_3), 4.3 (s, CH_2Br), 5.3 (s, CH_2OOC), 6.3–6.7 (2 aromatic H), 8.9 (s, 2 aromatic H), 9.2 (s, 1 aromatic H). The extent of esterification determined by comparing the area of the signal at 4.3 ppm with the area of the signal at 5.3 ppm was 0.13 esterified benzylic group per structural unit.

PPO esterified with potassium *N*-carbazolylacetate: ^{1}H NMR ($CHCl_3$-*d*, ppm) 2.1 (s, CH_3), 4.3 (s, CH_2Br), 4.75 (s, CH_2O), 5.0 (s, NCH_2), 6.3–6.7 (2 aromatic H), 7.0–7.6 (m, 6 aromatic H), 8.1 (d, 2 aromatic H). The extent of esterification was determined by comparing the area of the signal at 4.3 ppm with the area of the signal at 4.75.

PPO esterified with tetrabutylammonium 2-(*N*-carbazolyl)propionate: ^{1}H NMR ($CHCl_3$-*d*, ppm) 2.1 (s, CH_3), 2.7 (s, CH_2COO), 4.35 (m, CH_2Br, $COOCH_2O$), 4.9 (s, NCH_2), 6.3–6.7 (2 aromatic H), 7.0–7.6 (m, 6 aromatic H), 8.1 (d, 2 aromatic H). The extent of esterification was determined by first calculating the area of the signal at 6.3–6.7 ppm that was due to nonesterified structural units; i.e., the area of the signals from 7.0 to 8.1 ppm was multiplied by the ratio of esterified methyl protons to aromatic carbazole protons (2:8), that value was subtracted from the total area of the signal at 6.3–6.7 ppm, and the remainder was divided by the total area at 6.3–6.7 ppm. From this, the moles of esterified benzylic groups per structural unit was calculated to be 0.12.

Table I summarizes the reaction conditions and results of esterification of PPO for all reactions performed.

I. Esterification of PECH with Potassium *N*-Carbazolylacetate ($CzCH_2COO$–PECH) and Potassium *N*-Carbazolylpropionate ($CzCH_2CH_2COO$–PECH). In a typical procedure, PECH (2 g, 21 mmol Cl) was dissolved in Me_2SO (20 mL), and TBAH (0.50 g, 1.5 mmol) and potassium *N*-carbazolylacetate (4.2 g, 16 mmol) were added. The reaction mixture was stirred at 60 °C for 24 h and poured into methanol (150 mL). The obtained polymer was purified by precipitation from acetone solution into water and from acetone solution into methanol: ^{1}H NMR ($CHCl_3$-*d*, ppm) 2.5–4.2 (m, CH_2O, CH, CH_2Cl, CH_2OOC), 4.9 (s, NCH_2), 6.9–7.5 (m, 6 aromatic H), 8.0 (d, 2 aromatic H). The extent of esterification was determined by first calculating the area of the signals from 2.5 to 4.2 ppm that was due to nonesterified structural units; i.e., the area of the signals from 6.9 to 8.0 ppm was multiplied by the ratio of PECH protons to aromatic protons (5:8), that value was subtracted from the total area of the signals from 2.5 to 4.2 ppm, and the remainder was divided by the total area of the signals from 2.5 to 4.2 ppm. From this, the moles of esterified methyl groups per structural unit was calculated to be 0.16.

PECH esterified with potassium *N*-carbazolylpropionate ^{1}H NMR ($CHCl_3$-*d*, ppm) 2.7 (s, CH_2COO), 3.0–3.8 (m, CH_2O, CH, CH_2Cl), 3.9 (s, CH_2OOC), 4.5 (s, NCH_2, 7.0–7.5 (m, 6 aromatic H), 8.05 (d, 2 aromatic H). The extent of esterification was determined by first calculating the area of signals from 3.0 to 4.2 ppm that was due to nonesterified structural units; i.e., the area of the signals from 7.0 to 8.05 ppm was multiplied by the ratio of PECH protons to aromatic protons (5:8), that value was subtracted from the total area of the signals from 3.0 to 4.2 ppm, and the remainder was divided by the total area of the signals from 3.0 to 4.2 ppm.

Table I
Reaction Conditions and Results of Synthesis of PPO Containing Donor or Acceptor Groups[a]

nucleophile	mol of nucleophile	reacn time, h	mol fract of struct units containing $-CH_2Br$	% CH_2Br functionalized
$CzCH_2COONBu_4$	3.8	24^b	0.53	21
$CzCH_2COOK$	1.4	24^b	0.84	59
	3.5	2	0.53	66
	3.5	3	0.53	79
	3.5	4	0.53	100
$CzCH_2COOK$	3.5	7	0.53	100
	1.0	4	0.53	51
	1.0	8	0.53	77
	1.0	12	0.53	81
	0.9	24	0.14	43
$CzCH_2CH_2COONBu_4$	1.3	24^b	0.53	21
$DNCOONBu_4$	3.5	24^b	0.53	74
DNCOOK	1.5	24^b	0.84	14
	3.8	2	0.53	17
	3.8	3	0.53	19
	3.8	4.5	0.53	40
	3.8	7	0.53	68
	1.0	3.5	0.53	15
	1.0	7	0.53	24
	1.0	8	0.53	26
	1.0	20	0.53	53
	1.0	24	0.53	87
	1.1	24	0.23	43
	1.6	26.5	0.52	92

[a] TBAH concentration was 10% that of the potassium salts. Temperature was 60 °C except where indicated that it was 25 °C. Toluene was used as solvent for the potassium salts, THF for $CzCH_2COONBu_4$, and $CHCl_3$ for $CzCH_2CH_2COONBu_4$ and $DNCOONBu_4$. [b] Temperature was 25 °C.

J. Substitution of PECH with Carbazole (Cz-PECH). PECH was substituted with carbazole by dissolving 0.6 g of PECH (6.5 mmol Cl) in DMF (100 mL) and adding 50% NaOH (2.6 mL), 0.11 g of TBAH (0.32 mmol), and 1.6 g of carbazole (9.7 mmol) according to a method developed by N'Guyen et al.[19] The reaction mixture was stirred at 60 °C for 3 h and poured in aqueous methanol. The obtained polymer was purified by reprecipitation from chloroform into aqueous methanol and from chloroform into methanol: ^1H NMR ($CHCl_3$-*d*, ppm) 3.1–4.0 (m, CH_2O, CH, CH_2Cl, NCH_2), 7.0–7.5 (m, 6 aromatic H), 8.1 (d, 2 aromatic H). The extent of substitution was determined by first calculating the area of the signal at 3.1–4.0 ppm that was due to nonsubstituted structural units; i.e., the area of the signals from 7.0 to 8.1 ppm was multiplied by the ratio of PECH protons to aromatic protons (5:8), that value was subtracted from the total area of the signal at 3.1–4.0 ppm, and the remainder was divided by the total area of the signal at 3.1–4.0 ppm. From this, the moles of substituted methyl groups per structural unit was calculated to be 0.30.

K. Esterification of PECH with Tetrabutylammonium 2-(*N*-Carbazolyl)propionate ($CzCH_2CH_2COO$-PECH). PECH (1 g, 11 mmol of Cl) was dissolved in Me_2SO (10 mL), and tetrabutylammonium 2-(*N*-carbazolyl)propionate (1.7 g, 3.5 mmol) was added. The reaction mixture was stirred at 60 °C for 50 h and poured into methanol (150 mL). The obtained polymer was purified by reprecipitation from acetone into methanol: ^1H NMR ($CHCl_3$-*d*, ppm) 2.85 (s, CH_2COO), 3.1–3.9 (s, CH_2O, CH, CH_2Cl), 4.0 (s, CH_2OOC), 4.6 (s, NCH_2), 7.0–7.5 (m, 6 aromatic H), 8.05 (d, 2 aromatic H). The extent of esterification was determined as in section I.

Table II presents the reaction conditions and results of substitution of PECH for all reactions performed.

L. Techniques. ^1H NMR spectra (60 MHz) were recorded on a Varian EM-360 instrument. All spectra were obtained from $CHCl_3$-*d* or $(CH_3)_2CO$-d_6 solutions with Me_4Si as internal standard. A Digilab FTS-14 FTIR spectrometer was used to record IR spectra from KBr pellets. Glass transition temperatures (T_g) and changes in heat capacity at the glass transition temperatures (ΔC_p) were determined by a Perkin-Elmer differential scanning calorimeter (Model DSC-4) at a heating rate of 20 °C/min. Indium was used as calibration standard. The T_g values in Tables IV and V were recorded during the second and third (or greater) heating cycles, respectively. Number-average and weight-average molecular weights were determined by GPC.[1]

Table II
Reaction Conditions and Results of Synthesis of PECH Containing Donor Groups[a]

	mol per mol of $-CH_2Cl$			
nucleophile	nucleophile	TBAH	reacn time, h	% CH_2Cl functionalized
carbazole	1.5	0.05	3	30
$CzCH_2COOK$	0.75	0.08	3.5	6
	0.75	0.08	6	8
	0.75	0.08	9.5	11
	0.75	0.08	21	16
	0.75	0.08	24	18
	0.74	0.07	24	16
	0.75	0.07	23.5	22
$CzCH_2CH_2COOK$	0.75	0.08	49	28
	0.75	0.08	109	37
$CzCH_2CH_2COONBu_4$	0.50	0	6	5
	0.50	0	17	9
	0.50	0	20	9
	0.50	0	24	9
	0.50	0	41	13
	0.32	0	50	8

[a] DMF was used as solvent with carbazole, Me_2SO in all other reactions.

Results and Discussion

The synthetic route used for the chemical modification of PPO and PECH is outlined in Scheme I. The results of the esterification reactions of PPO are summarized in Table I. They show that both *N*-carbazolylacetate and 3,5-dinitrobenzoate groups can be incorporated into PPO using a solid–liquid phase-transfer system in a nonpolar solvent. This is in contrast to conventional nucleophilic substitutions, which require aprotic dipolar solvents. Since PPO is not soluble in aprotic dipolar solvents, the only available procedure for this reaction is that presented in the Experimental Section. In addition, the tetrabutylammonium salts of 2-(*N*-carbazolyl)propionate, *N*-carbazolylacetate, and 3,5-dinitrobenzoate were also used according to a non-phase-transfer system described by Shih et al.[20] In this case, a polar solvent was used to facilitate the displacement. Because these are the salts formed in phase-transfer catalysis, it is expected that they would be more reactive than the corresponding potassium salt used in phase-transfer reactions. This appears to be true in the case of 3,5-dinitrobenzoate (74% vs. 14% of the bromobenzylic groups were esterified) but is not true in the case of *N*-carbazolylacetate (21% vs. 60% of the bromobenzylic groups were esterified). That is, it is true in the case of weak nucleophiles but not in the case of strong nucleophiles. However, the tetrabutylammonium and potassium salt reactions are not directly comparable in either case because different proportions of nucleophile to Br were used and because PPO samples brominated to different degrees were used.

Figures 1 and 2 respectively show the conversion vs. time for substitution by potassium *N*-carbazolylacetate and by potassium 3,5-dinitrobenzoate on PPO. Figure 1 shows that substitution by potassium *N*-carbazolylacetate levels off with time, but by using a high enough concentration of nucleophile, it is possible to get 100% substitution of bromobenzylic groups in only 3 h. Figure 2 shows that substitution by potassium 3,5-dinitrobenzoate neither

Table III
Synthesis of PPO and PECH Containing Donor or Acceptor Groups Used in the Preparation of Polymer Blends[a]

		mol per mol of $-CH_2X$[b]			mol fract of struct units containing donor or acceptor groups
polym	nucleophile	nucleophile	TBAH	reacn time, h	
PPO (0.14-CH_2Br)	DNCOOK	1.6	0.31	69	0.08
PPO (0.23 -CH_2Br)		1.9	0.25	66	0.23
PPO (0.53 -CH_2Br)		1.6	0.10	26.5	0.48
PECH	carbazole	1.5	0.05	1	0.11
		1.5	0.05	2	0.27
PECH $CzCH_2COOK$		0.7	0.07	10	0.11
		0.8	0.07	23.5	0.22
		0.7	0.07	120	0.37
PECH $CzCH_2CH_2COOK$		0.8	0.08	49	0.28
		0.8	0.08	109	0.37

[a] All reactions were performed at 60 °C. [b] X = Br or Cl.

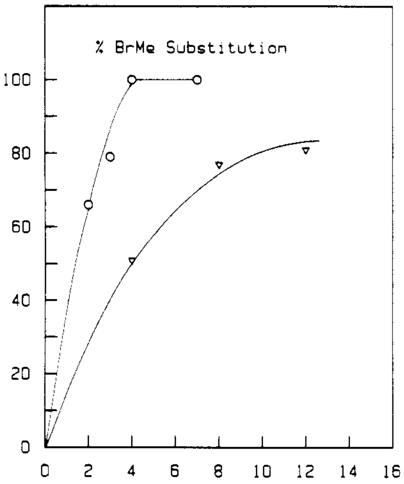

Figure 1. Conversion vs. time for esterification of PPO containing 0.53 molar fraction $-CH_2Br$ groups by 3.5 mol (○) and 1.0 mol (▽) potassium *N*-carbazolylacetate per mol $-CH_2Br$ at 60 °C in toluene.

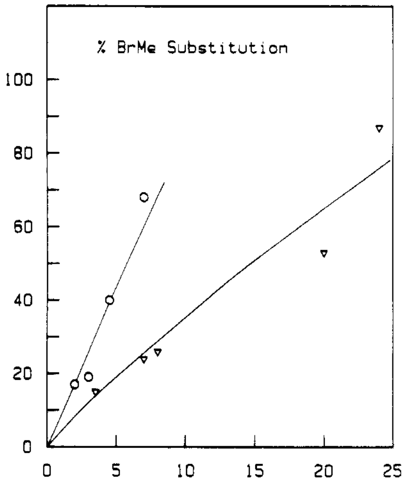

Figure 2. Conversion vs. time for esterification of PPO containing 0.53 molar fraction $-CH_2Br$ groups by 3.8 mol (○) and 1.0 moles (▽) potassium 3,5-dinitrobenzoate per mol $-CH_2Br$ at 60 °C in toluene.

levels off nor reaches 100% substitution of bromobenzylic groups during the time period studied. In addition, the last entry in Table I shows that 92% 3,5-dinitrobenzoate substitution has been reached after 26.5 h at 60 °C using 1.6 mol of nucleophile per mol of bromobenzylic group. Therefore, to reach a desired concentration of 3,5-dinitrobenzoate groups per PPO structural unit, it is necessary either to use a higher nucleophile concentration and/or reaction time or to use a PPO of higher CH_2Br content than is necessary. However, the unreacted bromobenzylic groups may influence the interactions between polymers in the blends made.

The results of the substitution reactions of PECH are summarized in Table II and plotted in Figure 3. They show that PECH is less reactive toward nucleophilic displacement than PPO. This is as expected because the chloromethyl groups from PECH are less electrophilic than the bromobenzylic groups from PPO both because bromine is a weaker base and therefore a better leaving group than chlorine and because benzylic halogens are more easily displaced than primary halogens. Therefore, all reactions must be performed at elevated temperatures, with no reaction occurring at room temperature. In addition, we found that potassium 3,5-dinitrobenzoate reacts with PECH in only trace amounts at 60 °C even after long reaction times.

The reaction conditions finally used to obtain the modified PPO and PECH polymers used in the blend study are shown in Table III.

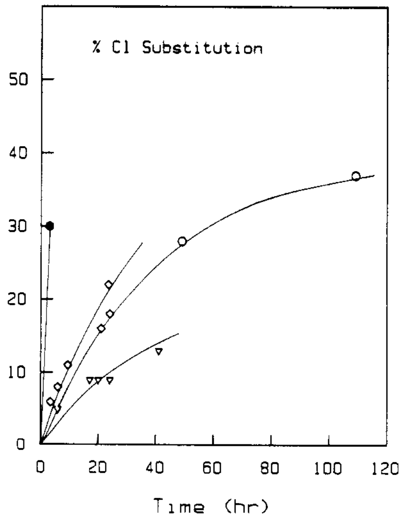

Figure 3. Conversion vs. time for esterification of PECH by 1.5 mol carbazole (●), 0.75 mol potassium *N*-carbazolylacetate (◇), 0.75 mol potassium *N*-carbazolylpropionate (○), and 0.50 mol tetrabutylammonium 2-(*N*-carbazolyl)propionate (▽) per mole $-CH_2Cl$ at 60 °C in the solvent designated in Table II.

The existence of a single glass transition at a temperature intermediate between those of the two-component polymers was used as a test for miscibility in the polymer–polymer blends. Table V shows the glass transition temperatures of polymers blended in a 1:1 molar ratio of

Table IV
Glass Transition Temperature of Blend Components

substit	mol fraction of struct units containing donor or acceptor groups	T_g, °C
	Modified PECH	
none		-32
Cz-	0.11	-06
	0.27	-11
$CzCH_2COO$-	0.09	-08
	0.22	16
	0.37	38
$CzCH_2CH_2COO$-	0.28	2
	0.37	27
	Modified PPO	
none		214
DNCOO-	0.09	198
	0.23	190
	0.46	169
Br	0.53	200

donor to acceptor groups, while Table IV shows the glass transition temperatures of the component polymers. Miscible blends of dinitrobenzoate-substituted PPO with substituted PECH were obtained with PECH containing as low as 0.37, 0.37, and 0.27 molar fraction of 2-(*N*-carbazolyl)propionate, *N*-carbazolylacetate, and carbazolyl, respectively. In addition, Table V shows that miscible blends can be obtained from PECH containing only 0.2–0.4 molar fraction donor groups and PPO containing 0.5 molar fraction acceptor groups. In such cases, an excess of PECH backbone polymer is required to maintain a 1:1 molar ratio of donor to acceptor groups. The ability to form miscible blends between highly substituted PPO and PECH with only low substitution is advantageous because of PECH's relative unreactiveness. Also, the shift in the two T_g's of the eighth entry in Table V shows that there are indeed interactions between the 2-(*N*-carbazolyl)propionate and 3,5-dinitrobenzoate groups in this system, even though the blend has phase-separated.

It appears that miscibility decreases as the distance between the complexing group and the polymer backbone increases. Therefore, interpolymer donor–acceptor complexes must either hold the two homopolymer backbones close enough together or be in significant abundance to prevent them from phase separating. To confirm this conclusion, the T_g–composition behavior was studied for blends of PECH containing 0.27 molar fraction carbazolyl (0.27 Cz–PECH) and PPO containing 0.23 molar fraction 3,5-dinitrobenzoate (0.23 DNCOO–PPO) and for blends of PECH containing 0.37 molar fraction 2-(*N*-carbazolyl)propionate (0.37 $CzCH_2CH_2COO$–PECH) and 0.23 DNCOO–PPO.

It is interesting to note that decomplexing endotherms are not observed in the first differential scanning calorimetry (DSC) of the modified PPO–PECH blends used in this study, in contrast to the comparatively strongly interacting systems observed in the previous study from this laboratory.[1] The previously studied systems have contained donor and acceptor groups in each structural unit. When the polymer architecture did not allow a proper donor–acceptor interchain interaction to occur, an endothermal decomplexation was observed. Such a system behaves in a similiar way to one presenting a lower critical solution temperature and can be considered as a model for determining thermodynamic parameters from DSC measurements. In the present case, decomplexation is apparently not occurring below the decomposition temperature. This is also evidenced by the fact that the miscible systems do not show phase separation in further heating scans after having been quenched. The random distribution of donor and acceptor groups on the PPO and PECH backbones apparently allows a better matching of the donor and acceptor groups in the EDA complex. This could have two consequences: an increase in the equilibrium constant of the EDA complex, and/or the formation of an EDA complex with a different conformation. Both avenues may enhance the strength of the donor–acceptor interactions since an increase of the equilibrium constant will increase the concentration of donor–acceptor pairs present in the EDA complex, while a different conformation could decrease the ionization potential value of the donor groups. This can be achieved by the participation of the highest occupied molecular orbital in the EDA complex being favored over that of the penultimate orbital,[1] enhancing the strength of the EDA complex. However, additional work is required to support these assumptions.

The dependence between the single glass transition temperature of the blends and their composition was analyzed by five classic equations available in the literature. These equations are summarized in Table VI, where T_g, T_{g_1}, and T_{g_2} are respectively the glass transition temperatures of the blend, homopolymer 1, and homopolymer 2, and w_1 and w_2 are the corresponding weight fractions. The parameter k in the Gordon–Taylor equation and in Kwei's equation is the ratio between the volume expansion coefficients of the homopolymers. The parameter b in the Jenckel–Heusch equation is empirical and varies from system to system. In Couchman's equation, ΔC_{p_1} and ΔC_{p_2} are the change in the heat capacity of the polymers 1 and 2 at their T_g. The quadratic term qw_1w_2 in Kwei's equation is assumed to be proportional to the number of specific interactions between the two polymers, q being a constant. In our case it could be interpreted as the contribution of the EDA interchain interaction. When $k = 1$

$$T_g = w_1T_{g_1} + w_2T_{g_2} + qw_1w_2$$

and this equation is identical with the Jenckel–Heusch equation, with $q = b(T_{g_1} - T_{g_2})$.

Table V
Glass Transition Temperatures of Blends of Modified PECH and Modified PPO

blend components				
substituent	mol fract of struct units containing donor groups	substituent	mol fract of struct units containing acceptor groups	T_g, °C
Cz-	0.11		0.09	-4, 190
	0.27	DNCOO-	0.23	74
	0.27		0.46	65
$CzCH_2COO$-	0.09		0.09	-5, 190
	0.22		0.23	17, 182
	0.37	DNCOO-	0.46	80
	0.22		0.46	55
$CzCH_2CH_2COO$-	0.28		0.23	20, 165
	0.37	DNCOO-	0.23	44
	0.37		0.46	54

Table VI
Equations Describing T_g Variation with Composition for Miscible Blends

eq	parameter: 0.27 Cz-PECH + 0.23 DNCOO-PPO[a]	parameter: 0.37 CzCH$_2$CH$_2$COO-PECH + 0.23 DNCOO-PPO[b]
Gordon-Taylor[c] $T_g = \dfrac{w_1 T_{g_1} + k w_2 T_{g_2}}{w_1 + k w_2}$	$k = 0.55$	$k = 0.10$
Fox[d] $\dfrac{1}{T_g} = \dfrac{w_1}{T_{g_1}} + \dfrac{w_2}{T_{g_2}}$		
Jenckel-Heusch[e] $T_g = w_1 T_{g_1} + w_2 T_{g_2} + w_1 w_2 b(T_{g_1} - T_{g_2})$	$b = 0.76$	$b = 1.81$
Couchman[f] $\ln T_g = \dfrac{w_1 \Delta C_{p_1} \ln T_{g_1} + w_2 \Delta C_{p_2} \ln T_{g_2}}{w_1 \Delta C_{p_1} + w_2 \Delta C_{p_2}}$	$\Delta C_{p_1} = 0.055$ $\Delta C_{p_2} = 0.053$	$\Delta C_{p_1} = 0.081$ $\Delta C_{p_2} = 0.053$
Kwei[g] $T_g = \dfrac{w_1 T_{g_1} + k w_2 T_{g_2}}{w_1 + k w_2} + q w_1 w_2$	$k = 1.0, q = -151.85$	$k = 0.11, q = -16.36$

[a] $T_{g_1} = -11$ °C, $T_{g_2} = 190$ °C. [b] $T_{g_1} = 27$ °C, $T_{g_2} = 190$ °C. [c] Reference 21. [d] Reference 23. [e] Reference 22. [f] References 24 and 25. [g] Reference 26.

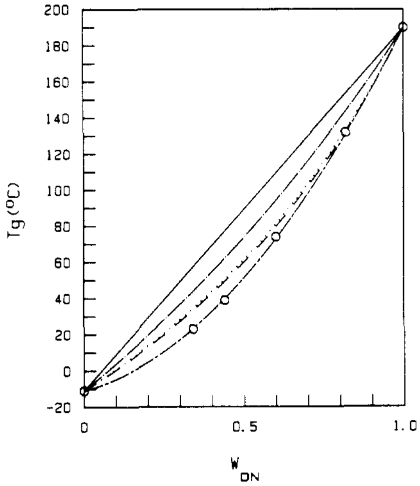

Figure 4. Experimental T_g values for the system 0.27 Cz-PECH + 0.23 DNCOO-PPO, and T_g values as predicted by the Gordon–Taylor (- - -), Fox (...), Jenckel–Heusch (— — —), and Couchman (—·—) equations.

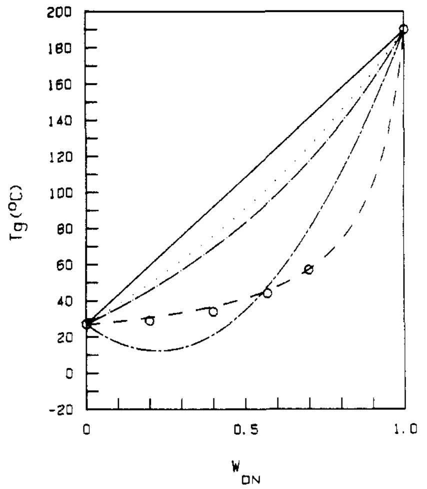

Figure 5. Experimental T_g values for the system 0.37 CzCH$_2$CH$_2$COO-PECH + 0.23 DNCOO-PPO, and T_g values as predicted by the Gordon–Taylor (- - -), Fox, (...), Jenckel–Heusch (— — —), and Couchman (—·—) equations.

Both the k value from the Gordon–Taylor equation and the q value from Kwei's equation are used in the literature to estimate the strength of the interchain interaction. For a detailed discussion on this subject see the previous paper.[1]

Table VI also shows the parameter values predicted by the various equations as determined by standard least-squares procedures to obtain the best fit with experimental points. Figures 4 and 5 show the glass transition temperatures of the blends of 0.23 Cz-PECH and 0.37 CzCH$_2$CH$_2$COO-PECH with 0.23 DNCOO-PPO, respectively, as well as the values predicted by the Gordon–Taylor, Fox, Jenckel–Heusch, and Couchman equations. The values predicted for both systems by Kwei's equation are plotted in Figure 6. These figures demonstrate that the best fit with experimental points is obtained from Kwei's equation with $k = 1$ and $q = -151.85$ for the Cz-PECH + DNCOO-PPO system and $k = 0.11$ and $q = -16.36$ for the CzCH$_2$CH$_2$COO-PECH + DNCOO-PPO system. Comparison of Figures 4 and 6 demonstrates that since $k = 1$ in the Cz-PECH + DNCOO-PPO system, the

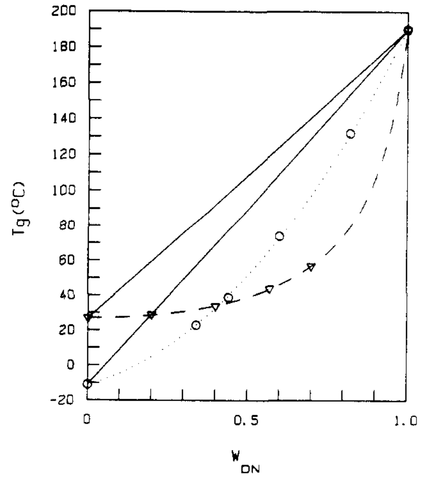

Figure 6. Experimental T_g values and T_g values as predicted by Kwei's equation for the 0.27 Cz-PECH–0.23 DNCOO-PPO (...) and 0.37 CzCH$_2$CH$_2$COO-PECH + 0.23 DNCOO-PPO (- - -) systems.

same fit is obtained from the Jenckel–Heusch equation with $b = 0.76$. This is not true for the $CzCH_2CH_2COO$–PECH + DNCOO–PPO system since a second parameter ($k = 0.11$) is needed to even match the shape of the T_g dependence on composition.

As discussed previously,[1] there are two possible indications of the strength of interchain interactions. One possibility is that the q value from Kwei's equation is increasingly positive as the strength of the interaction increases. The other indication as demonstrated by UV absorbance is an increasingly positive deviation of blend glass transition temperature from weight-average values. Since $k = 1$ for the Cz–PECH + DNCOO–PPO system, its negative q value can be compared to the positive q values of the homopolymer EDA complexes studied previously[1] to demonstrate that PPO and PECH in this system are only weakly interacting. Although the $CzCH_2CH_2COO$–PECH + DNCOO–PPO system cannot be directly compared with these other systems through its q value because of a different optimum value of k, it can be qualitatively compared by its deviation of glass transition temperature from the weight-average values. In this case, the deviation is negative. Since this deviation is negative to a greater extent than Cz–PECH + DNCOO–PPO, the interchain interactions are apparently weaker, supporting the earlier conclusion that miscibility decreases as the distance between the complexing group and the polymer backbone increases.

Although we have encountered negative deviations in several other systems,[27] we cannot at this time provide any conclusive explanation for a negative q value in Kwei's equation. Further work is required to elucidate this behavior and is in progress in our laboratory.

Conclusions

Interchain EDA interactions can be introduced in originally nonmiscible polymers to induce miscibility. This can be accomplished by the nucleophilic displacement of halogen on polymer backbones by potassium salts of carbazoyl- and 3,5-dinitrobenzoyl-containing carboxylic acids under phase-transfer-catalyzed reaction conditions. In the case of PPO and PECH, miscibility is obtained when the two backbones contain donor and acceptor groups in at least 25% of the structural units. However, miscibility is more easily induced by using fewer methylene spacers between the polymer backbone and the EDA interacting group. Of several equations available in the literature for describing the relationship between blend T_g and composition, Kwei's equation gives the best fit with experimental points of the Cz–PECH + DNCOO–PPO and $CzCH_2CH_2COO$–PECH + DNCOO–PPO systems.

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