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Interchain Electron Donor–Acceptor Complexes: A Model To Study Polymer–Polymer Miscibility?†

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ABSTRACT: Interpolymeric interactions based on electron donor–acceptor (EDA) complexes were used to study polymer miscibility. A new series of comblike polymers containing the electron donor carbazole moiety in the side chain, poly((*N*-alkylcarbazol-3-yl)methyl methacrylates) (PHMCM-*n*) with n = 1–16 (number of carbon atoms in the alkyl group), were synthesized, and their interpolymeric EDA complexes with an acceptor polymer, i.e., poly(2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate) (PDNBM), were studied by differential scanning calorimetry and compared with EDA complexes of poly(2-carbazol-*N*-ylethyl methacrylate) (PHECM). Blends of all donors and acceptor polymers show a single T_g as prepared, but only the lower homologues of the series are miscible under different thermal conditions. In the case of PHMCM-2 blends an endotherm of "decomplexation" is observed, and this system could be considered as one showing lower critical solution temperature. The glass-transition temperatures of the miscible systems depend on the composition of the blends and show large positive deviations from the weight-average values. This indicates the formation of thermally reversible cross-linked networks. Different equations available in the literature to correlate glass-transition temperatures of miscible blends with their composition were tested on these systems.

Introduction

Nonbonding type interactions are responsible in most cases for the self-organization of both natural and synthetic macromolecules. The current situation on the role of nonbonding interactions in chemistry has been recently discussed by Lord A. R. Todd: "Apart from consideration of the hydrogen bond, we organic chemists have really paid little attention to linkages other than purely covalent. I believe that it will be the duty of organic chemists in the future to study the weak, non-bonding interactions which are of enormous importance in the large natural macromolecules. Such studies will lead to a blossoming of organic chemistry in the future" (from Lord Alexander R.

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† This paper is dedicated to Professor Herman F. Mark on the occasion of his 90th birthday.

0024-9297/86/2219-0055$01.50/0

Todd Lecture, "Chemie in Vergangenheit und Gegenwart", delivered on the occasion of the presentation of the "Goldenes Doktordiplom", Universitat Frankfurt, Oct 16, 1981).

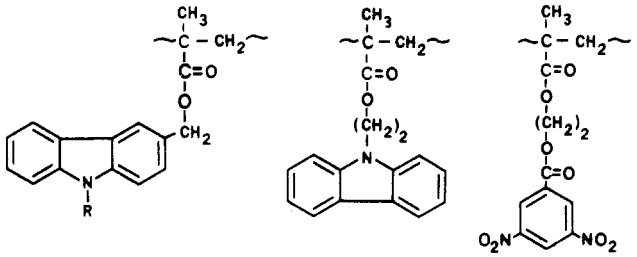
Indeed, to answer questions like "why do molecules interact" or "which is the origin of electron donor–acceptor (EDA) complexes, hydrogen bonding or proton affinity" is not yet a very simple task, even in the case of very simple compounds.[1] In EDA complexes the nonbonding interaction is not dominated by charge transfer (CT) only. At the same time, hydrogen bonding has an important CT contribution.[1] In an attempt to obtain some insight on the role of nonbonding interactions on polymer synthesis as well as polymer morphology and properties, we decided to use EDA interactions as a model. Several reasons for this selection are as follows. Both electron donor and electron acceptor type compounds do not self-interact, while in most cases hydrogen bonding compounds do. At least for weak EDA interactions, their bond energy should depend on the ionization potential of the donor, on the electronic affinity of the acceptor, and on the EDA complex conformation.[2]

In a previous series of publications, we have pointed out some of the implications of EDA complexes in copolymerization,[3] and also demonstrated that both intra- and interchain EDA interactions strongly affect the copolymer properties.[4] Although the role of intermonomeric EDA complexes in both the initiation and propagation steps of copolymerization have been under study for about 30 years,[5] only the initiation step has been recently explained.[6] The possible role of intermonomeric EDA complexes in the propagation step has been recently reviewed.[7]

When we study the role of intermonomeric EDA complexes in the propagation step of copolymerization and especially the effect of intrachain interactions on the physical properties of such a copolymer, it is important to consider the following possibilities in the selection of monomers. First, select a monomer pair for which the initiation of polymerization is not through the spontaneous "bond forming initiation concept",[6] and this could be done by choosing a pair of acrylates or methacrylates. Second, the D–A monomer pair should give strong intermonomeric EDA interactions, and after copolymerization strong intrachain interactions, but not interchain EDA interactions. This D–A monomer pair would let us not only gain some insight on the role of intermonomeric EDA complexes in the propagation step of copolymerization but also understand how strong intrachain EDA interactions, free from interchain interactions, affect the physical properties of the obtained polymer. To develop such a copolymerization system is the first goal of this paper.

It has not been accepted until recently that polymer miscibility,[8-12] wettability, adsorption, adhesion, reinforcement, and mechanical and many other properties[8,9] are controlled by polymer–polymer interactions. Although two of the most elegant techniques to study polymer miscibility are based on the use of nonradiative energy transfer[15-17] and exciplex emission[18] phenomena between polymers labeled with D and A groups, there is little information in the literature concerning the use of interchain EDA complexes in the study of interpolymeric interactions and their eventual use in the preparation of miscible polymer blends.[2,4,19-25]

It is the second goal of this paper to present a systematic study of interchain EDA complexes between a series of carbazole-containing polymers and an electron-acceptor polymer. The electron-donor polymers used in this study were poly(2-carbazol-*N*-ylethyl methacrylate) (PHECM) and a homologous series of poly([*N*-alkyl carbazol-3-yl)-methyl methacrylates] (PHMCM-*n*). The electron-acceptor polymer was poly(2-((3,5-dinitrobenzoyl)oxy)ethyl methacrylate) (PDNBM). The structures of these polymers are shown below. The strength of the interchain



PHMCM-n PHECM PDNBM

EDA interactions could be easily tailored by changing the length of the alkyl side chain in the donor polymers.

Experimental Section

Materials. Carbazole (Lancaster Synthesis) was purified by several recrystallizations from ethanol. 2,2′-Azoisobutyronitrile (AIBN) (Fluka) was recrystallized from methanol below 40 °C. 1,4-Dioxane (Aldrich) used as polymerization solvent was refluxed over sodium and distilled under argon. All other reagents were used as received.

Techniques. ^{1}H NMR spectra (200 MHz) were recorded on a Varian XL-200 spectrometer in $CDCl_3$ solutions with Me_4Si as internal standard. Thermal transitions, changes in heat capacity at the glass-transition temperature, and enthalpy changes were determined with a Perkin-Elmer DSC-4 differential scanning calorimeter. Scans were run at 20 °C/min, and indium was used as a calibration standard. All glass-transition temperatures reported were read during the second or third heating cycle except as noted. Thermogravimetric analyses were performed with a Perkin-Elmer TGS-2 thermogravimetric analyzer at 20 °C/min. All homopolymers and EDA complexes were thermally stable at least up to 200 °C. Molecular weights were determined by gel permeation chromatography (GPC). GPC analyses were carried out in a Perkin-Elmer Series 10 LC equipped with LC-100 column oven, LC 600 autosampler, and Sigma 15 data station. The measurements were made by using an UV detector, THF as solvent (1 mL/min, 40 °C), a set of PL-gel columns of 10^2, 5×10^2, 10^3, 10^4, and 10^5 Å, and a calibration plot constructed with polystyrene standards. UV-visible spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer.

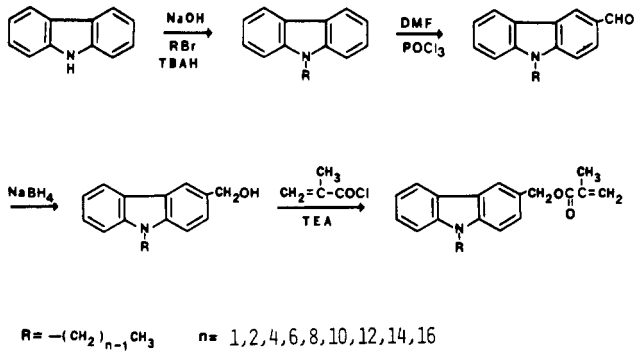
Synthesis of 2-Carbazol-*N*-ylethyl Methacrylate (HECM). HECM was prepared by esterification of *N*-(2-hydroxyethyl)-carbazole with methacryloyl chloride in dried THF and in the presence of triethylamine. *N*-(2-Hydroxyethyl)carbazole was synthesized from potassium carbazole and ethylene oxide. The detailed synthesis has been presented elsewhere.[27] After recrystallization from methanol, white crystals with mp 82–83 °C were obtained: ^{1}H NMR ($CDCl_3$) δ 1.78 (s, CH_3), 4.53 (s, $-NCH_2CH_2O-$), 5.40 and 5.73 (s, $CH_2 = C$), 7.0–7.5 (m, 6 aromatic protons), 7.9–8.1 (m, 2 aromatic protons).

Synthesis of 2-((3,5-Dinitrobenzoyl)oxy)ethyl Methacrylate (DNBM). DNBM was synthesized by esterification of 2-hydroxyethyl 3,5-dinitrobenzoate with methacryloyl chloride in dried THF in the presence of triethylamine. The detailed procedure has been reported elsewhere.[28] After recrystallization from methanol, crystals with mp 70–71 °C were obtained: ^{1}H NMR ($CDCl_3$) δ 2.00 (s, CH_3), 4.40–4.80 (m, $-OCH_2CH_2O-$), 5.63 and 6.18 (s, $CH_2 = C$), 9.27 (s, 3 aromatic protons).

Synthesis of (*N*-Alkylcarbazol-3-yl)methyl Methacrylates. The synthetic route used to prepare these monomers is outlined in Scheme I, and it follows a procedure developed for the synthesis of (*N*-ethyl-carbazol-3-yl)methyl methacrylate.[29] The following example illustrates the synthesis of these monomers.

Synthesis of *N*-Tetradecylcarbazole. Carbazole (20 g, 0.12 mol), powdered NaOH (7.2 g, 0.18 mol), 1-bromotetradecane (49.75

Scheme I



g, 0.18 mol), and tetrabutylammonium hydrogen sulfate (TBAH) (1.22 g, 3.6×10^{-3} mol) were added to 100 mL of acetone. The mixture was heated to reflux and stirred at this temperature for 15 h. The initially insoluble reaction mixture became clear at the end of the reaction. Finally the solution was poured into water, and the precipitate was filtered off, washed with water until of normal pH, and dried under vacuum. The product was further purified by recrystallization from isopropyl alcohol: mp 42–44 °C; yield, 91%.

Synthesis of *N*-Tetradecyl-3-formylcarbazole. To 6 g (0.0825 mol) of DMF at 0 °C, 12.65 g (0.0825 mol) of phosphorus oxychloride was added dropwise. The solution was allowed to warm up to room temperature, and 20 g (0.055 mol) of *N*-tetradecylcarbazole dissolved in 20 mL of *o*-dichlorobenzene was added. The reaction mixture was heated to 90 °C and left at this temperature overnight. It was then poured into water, and the precipitate was filtered, washed with water, and recrystallized from methanol: mp 81–83 °C; yield 85%; ^{1}H NMR ($CDCl_3$) δ 0.6–2.0 (m, C_{13} chain), 4.23 (t, $-CH_2-N$), 7.0–8.5 (m, 8 aromatic protons), 10.03 (s, -CHO).

Synthesis of *N*-Tetradecyl-3-carbazolemethanol. A solution of 1.64 g (0.043 mol) of $NaBH_4$ in 10 mL of 0.45 N aqueous NaOH was added dropwise to a stirred mixture of 17 g (0.043 mol) of *N*-tetradecyl-3-formylcarbazole in 400 mL of methanol. The mixture was stirred at room temperature until everything dissolved (about 1 h). Half the methanol was then evaporated and the solution poured into water. The product was filtered, dried under vacuum, and recrystallized from a 1:1 mixture (v/v) of benzene and cyclohexane: mp 72–74 °C; yield 90%; ^{1}H NMR ($CDCl_3$) δ 0.6–2.0 (m, C_{13} chain), 4.23 (t, $-CH_2N$), 4.75 (s, $-CH_2O-$), 7.0–8.1 (m, 8 aromatic protons).

Synthesis of (*N*-Tetradecylcarbazol-3-yl)methyl Methacrylate. *N*-Tetradecyl-3-carbazolemethanol (9 g, 0.023 mol) was dissolved in a mixture of 50 mL of dried THF and 4.55 mL (0.033 mol) of triethylamine dried over NaOH pellets. To the ice-water cooled solution, 3.19 mL (0.033 mol) of methacryloyl chloride were added dropwise, and the reaction mixture was stirred at room temperature overnight. At the end of the reaction, the triethylamine hydrochloride was filtered off, and the filtrate was poured into water. The precipitated product was filtered and dried under vacuum. It was further purified by recrystallization from methanol: mp 41–42 °C; yield 82%; ^{1}H NMR ($CDCl_3$) δ 0.6–2.0 (m, C_{13} chain and $CH_3-C=$), 4.23 (t, $-CH_2N$), 5.37 (s, $-CH_2O-$), 5.5 and 6.13 (s, $H_2C=C$), 7.0–8.1 (m, 8 aromatic protons).

The melting points and ^{1}H NMR spectra of the other monomers are summarized in Table I.

Polymerizations. All monomers were polymerized in dioxane by using AIBN as a radical initiator. Polymerizations were carried out in sealed glass ampules under argon atmosphere at 60 °C for 15 h. Monomer concentration was 10% (w/v), and initiator concentration was 1 wt % from the monomer. After the polymerization time, the reaction mixture was diluted with THF and precipitated into methanol. The filtered polymers were dried and purified by reprecipitation into methanol from THF solutions. The characterization of the obtained polymers is presented in Table II.

Preparation of Interchain EDA Complexes. Interchain EDA complexes were prepared either by mixing THF solutions of the D and A containing polymers, followed by slow evaporation of the solvent, or by thorough mixing of the solid states of the polymers in a mortar. When the EDA complexes were prepared from solution they were first dried under vacuum at room temperature for at least 24–48 h and then dried at different temperatures, which will be detailed in the Discussion section.

Table I
Characterization of (*N*-Alkylcarbazol-3-yl)methyl Methacrylates

PHMCM-*n*, *n*	mp, °C	^{1}H NMR (ppm)
1	63–65	2.00 (s, $CH_3C=C$), 3.82 (s, CH_3N), 5.43 (s, $-OCH_2-$), 5.60 and 6.21 (s, $CH_2=C$), 7.10–8.30 (m, 7 aromatic protons)
2	74–75	1.37 (t, CH_3), 1.98 (s, $CH_3C=C$), 4.27 (q, $-CH_2N$), 5.35 (s, $-OCH_2-$), 5.45 and 6.10 (s, $CH_2=C$), 7.00–8.10 (m, 7 aromatic protons)
4	68–70	0.70–2.00 (m, C_3 chain and $CH_3C=C$), 4.25 (t, $-CH_2N$), 5.40 (s, $-OCH_2-$), 5.52 and 6.13 (s, $CH_2=C$), 7.00–8.20 (m, 7 aromatic protons)
6	liquid	0.70–2.00 (m, C_5 chain and $CH_3C=C$), 4.22 (t, $-CH_2N$), 5.37 (s, $-OCH_2-$), 5.52 and 6.12 (s, $CH_2=C$), 7.00–8.20 (m, 7 aromatic protons)
8	liquid	0.70–2.00 (m, C_7 chain and $CH_3C=C$), 4.20 (t, $-CH_2N$), 5.34 (s, $-OCH_2-$), 5.48 and 6.12 (s, $CH_2=C$), 7.00–8.20 (m, 7 aromatic protons)
10	34–35	0.70–2.00 (m, C_9 chain and $CH_3C=C$), 4.22 (t, $-CH_2N$), 5.35 (s, $-OCH_2-$), 5.50 and 6.12 (s, $CH_2=C$), 7.00–8.20 (m, 7 aromatic protons)
12	33–34	0.70–2.00 (m, C_{11} chain and $CH_3C=C$), 4.28 (t, $-CH_2N$), 5.36 (s, $-OCH_2-$), 5.53 and 6.15 (s, $CH_2=C$), 7.00–8.20 (m, 7 aromatic protons)
14	41–42	0.70–2.00 (m, C_{13} chain and $CH_3C=C$), 4.20 (t, $-CH_2N$), 5.36 (s, $-OCH_2-$), 5.51 and 6.13 (s, $CH_2=C$), 7.00–8.15 (m, 7 aromatic protons)
16	47–49	0.70–2.00 (m, C_{15} chain and $CH_3C=C$), 4.20 (t, $-CH_2N$), 5.36 (s, $-OCH_2-$), 5.52 and 6.13 (s, $CH_2=C$), 7.00–8.15 (m, 7 aromatic protons)

Table II
Synthesis and Characterization of PHMCM-*n*, PHECM, and PDNBM

polymer	conversion/%	10^4M_n	10^4M_w	M_w/M_n	T_g/°C
PHMCM-1	77.0	1.83	2.66	1.46	144
PHMCM-2	95.0	3.69	12.15	3.29	134
PHMCM-4	86.0	1.76	6.08	3.46	93
PHMCM-6	54.1	3.01	10.80	3.58	72
PHMCM-8	87.9	2.48	8.12	3.28	55
PHMCM-10	94.9	2.58	8.62	3.34	40
PHMCM-12	92.5	4.27	11.40	2.67	33
PHMCM-14	91.8	3.93	15.30	3.90	29
PHMCM-16	87.9	3.26	10.20	3.12	28
PHECM	98.8	2.19	10.40	4.74	146
PDNBM	73.5	2.42	10.24	4.21	94

Results and Discussion

As we have mentioned in the introduction, the first goal of this paper is to tailor a D–A monomer pair that will provide strong intermonomeric EDA complexes and after copolymerization will give rise to intrachain EDA complexes only. Our approach was to synthesize a series of comblike carbazole-containing monomers with alkyl groups attached in such a way that the comblike polymer will not provide any side-chain crystallization. In this way the alkyl groups will give rise to interchain steric hindrances, thus reducing the interchain EDA complexation. This synthetic procedure will let us understand the behavior of an in-

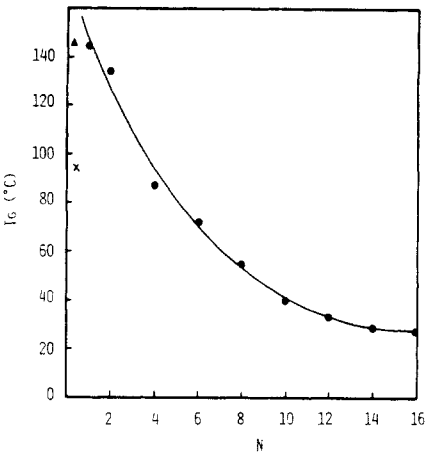


Figure 1. Glass-transition temperatures of PHMCM-*n* polymers vs. the number of carbon atoms in the alkyl side chain: (▲) PHECM; (x) PDNBM.

trachain charge transfer copolymer free of interchain EDA interactions. The interchain EDA interactions are apparently important when we discuss the properties of intrachain charge transfer complexes of random copolymers. Such a random copolymer would have to behave as a sequential copolymer in which the alternating coisotactic sequences might behave as thermally reversible ladder-type units. Classical work on comblike polymers clearly demonstrated that when the alkyl side chains contain more than 12 carbon atoms, side-chain crystallization occurs.[30-35] The structures of the synthesized polymers are outlined in the Introduction. It has been speculated that the nonsymmetrical attachment of the alkyl groups to the poly((*N*-alkylcarbazol-3-yl)methyl methacrylates) will not induce a side-chain crystallization. Indeed even polymers with 16 carbons in the side chain do not give rise to side-chain crystallization. The dependence of T_g on the number of carbons in the alkyl side chain is presented in Figure 1. The increase in the number of carbons in the side chain decreases the glass-transition temperature, which levels off for the polymers containing 14 and 16 carbons. It has to be clear that within the range of molecular weights presented in Table II, the T_g values are not dependent on polymer molecular weight. This was demonstrated by characterizing several polymer samples with molecular weights higher than 200 000.[36] The same is true for the PHECM and PDNBM samples used in this study.

Since the equilibrium constants of the charge-transfer complexes have little physical significance (for a detailed discussion see ref 2), only the ionization potentials of the donor polymers were determined. This was done by running the UV-vis spectra of the charge-transfer complexes of the donor polymers with an acceptor compound characterized in the literature. As it has been often demonstrated, in many cases the transition from both the highest and the second highest occupied molecular orbitals of the donor to the lowest empty molecular orbital of the acceptor[37-42] occur. These will give rise to the first (I_{p_1}) and second (I_{p_2}) ionization potentials. Their probability is not only thermodynamically controlled, but it strongly depends on the conformation of the EDA complex. In many EDA complexes the most probable transition is the least thermodynamically stable. This is especially true for the case of carbazole-containing compounds, and this behavior often leads to the misinterpretation of the I_p values.

This is the case when both transitions are overlapped in the absorption spectrum of the EDA complex, and they could be separated in several cases only by circular dichroism studies on chiral EDA complexes.[43,44] The behavior of the EDA complexes of our donor polymers with tetracyanoethylene (TCE) is a good example.

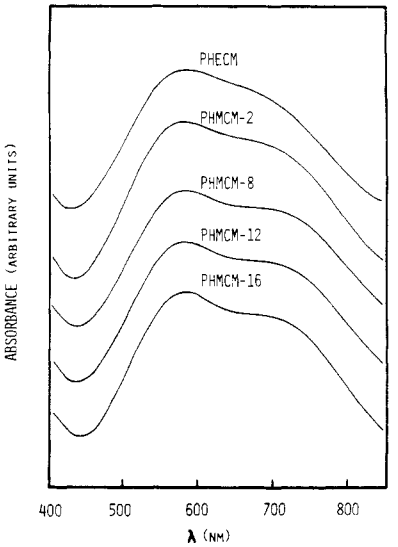


Figure 2. UV-vis spectra of the TCE complexes of some donor polymers (polymer concentration, 1.2×10^{-2} M; TCE concentration, 3×10^{-3} M).

Figure 2 shows the UV-vis spectra of the EDA complexes of PHECM and several PHMCM-*n* polymers with TCE. As can be seen in the figure, the spectra are very similar. All complexes show a maximum at 585 nm, which corresponds to an ionization potential I_{p_2} of 8.02 eV. The other maximum in the spectra is approximately at 710 nm, which would correspond to I_{p_1} = 7.60 eV. The ionization potentials were calculated by conventional methods described previously.[39,41,45] It is interesting to note that the second maximum is better resolved in the case of PHMCM-*n* than in PHECM, and the resolution seems to increase with the length of the alkyl side chain. This suggests a different conformation of the complexes of PHMCM-*n* compared to that of PHECM. Further research to elucidate this problem is in progress.

Solution Characterization of Interchain EDA Complexes. When solutions of PHECM or PHMCM-1 in THF are mixed with a solution containing an equimolar amount of PDNBM also in THF, a red precipitate of EDA complex is formed spontaneously. Even in very dilute solutions the EDA complexes are not soluble at the boiling point of THF.

For the comblike carbazole polymers with longer alkyl groups, dilute solutions of the interchain EDA complexes could be obtained. In fact, complexes of polymers with more than four carbon atoms in the side chain are soluble in THF at room temperature. At the same time with the increase in the length of the alkyl group the color of the EDA complex changes from red to light yellow.

Figure 3 presents the absorption of the CT band at 460 nm of these EDA complexes as a function of the number of carbon atoms in the alkyl side chain. This plot can be used as a qualitative estimation of the amount of D and A groups that participate in the EDA complex. Quantitative estimations are difficult to obtain, since the meaning of EDA complexes equilibrium constants is still controversial.[2] In our case the situation seems to be even more complicated if we assume that the length of the alkyl side chains might change the conformation of the EDA complex and not only its equilibrium constant. This would mean that equilibrium constants would be measured for completely different EDA complexes in each case.

Figure 3 shows a strong decrease in the absorption at 460 nm for the complexes of polymers containing more

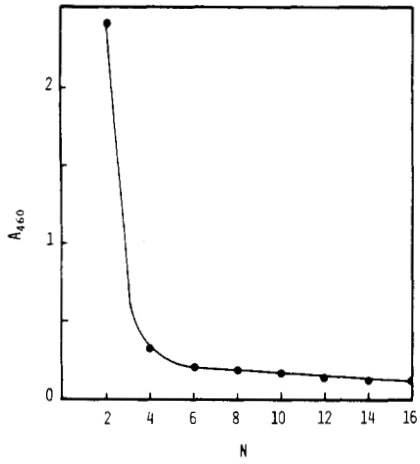


Figure 3. Absorbance at 460 nm of PHMCM-*n*-PDNBM EDA complexes. (Donor and acceptor concentration, 0.01 M in THF; T = 30 °C.)

than four carbon atoms in the side chain. This suggests that the interchain EDA interactions in these complexes are very weak in comparison to those having strong absorption in the spectrum or to those which precipitate from solution.

Solid-State Characterization of PHECM–PDNBM and PHMCM-1–PDNBM Complexes. A simple approach to the understanding of the interchain EDA interactions strength between the D and A polymers would be by studying their miscibility. The miscibility of a polymer mixture is controlled by the free energy of mixing, ΔG_{mix}, which is defined as

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

where ΔH_{mix} is the enthalpy change on mixing and ΔS_{mix} is the entropy change on mixing.[8,9] A miscible system should have a $\Delta G_{mix} \leq 0$. Since on mixing two polymers ΔS_{mix} is not large enough, the only way to have a negative free energy of mixing is by an exothermic mixing process (i.e., $\Delta H_{mix} < 0$). This usually occurs when the two polymers present interchain interactions within the range of the hydrogen bond strength (ΔH = 2–4 kcal/mol). It is well established that the formation of EDA complexes is an exothermal process and that their enthalpies of formation are within the range or even higher than those of the hydrogen bond, i.e., ΔH = 2–12 kcal/mol.[46-48] Consequently, it is expected that interchain EDA complexes would have to behave as miscible blends, and this behavior would be controlled through the strength of the D–A interaction.

A single T_g or a shift of the T_g of the parent polymers was used for the estimation of the polymer miscibility. The interchain EDA complexes were obtained by two different methods. The first one was a solid-state thorough mixing of the polymers in a mortar. The polymer mixture turned red very quickly. This indicates the formation of an EDA complex in the solid state. The second method was by mixing THF solutions of the two polymers. A precipitate forms immediately. The solvent was allowed to evaporate at room temperature, and the EDA complex was first dried at room temperature under vacuum to constant weight. The DSC scans of the EDA complexes prepared from solution showed a single T_g even during the first scan. The second scan of the solid state prepared complexes showed always a single T_g. A broad exotherm is sometimes observed in the first scan. This is due to the exothermal heat of mixing. No attempts to evaluate this exothermic process were made, since it is strongly dependent on the polymer mixing history. In poorly mixed systems, two T_g's are

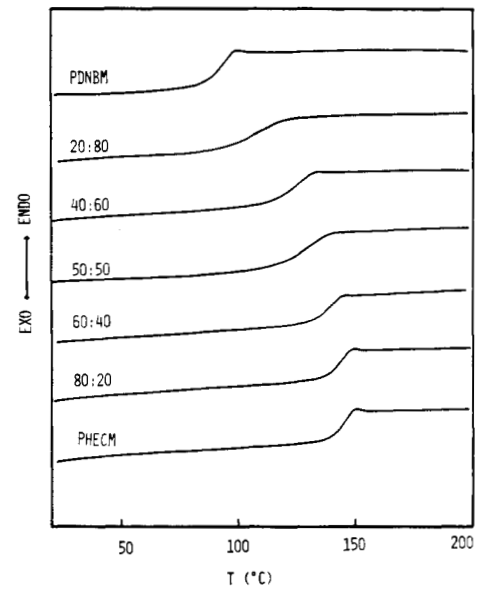


Figure 4. DSC traces of PHECM–PDNBM EDA complexes of different compositions, dried at 120 °C under vacuum. (PHECM/PDNBM weight ratio shown above the corresponding curve.)

observed, but a single T_g is obtained by annealing the mixture at 150 °C for different periods of time. Usually a poorly mixed mixture showed a single T_g after no more than 15 h of annealing at 150 °C.

The T_g values of the EDA complexes prepared from solution were always about 40 °C lower than those of the complexes prepared in solid state. These complexes were prepared several times in the same manner by using different polymer concentrations. Successive heating and cooling DSC scans always showed reproducible data. Annealing of these complexes in the DSC instrument did not change the T_g's of the solution-prepared complexes. To reach the value of the T_g of the solid state prepared complexes, it was necessary to dry the solution-prepared complexes for long times under vacuum at a temperature above T_g. We cannot explain the difference between the T_g's of the high-temperature and low-temperature dried solution complexes on the basis of free residual solvent in the mixture. Free solvent in the blend will not give reproducible T_g values. Apparently the donor character of THF induces the formation of a multiple EDA complex in which THF is weakly bonded in between the 3,5-dinitrobenzoyl and carbazolyl units. The D and A groups in this complex would have a different conformation than that of the solid state prepared complex, and in this way it would be possible to explain how only traces of THF would affect so much the T_g values. Additional discussions on this topic will be the subject of another paper from our laboratory.[49] DSC traces of the PHECM–PDNBM and PHMCM-1–PDNBM complexes are presented in Figures 4 and 5 (second scans). The T_g values corresponding to these DSC curves are tabulated in Table III.

There are several classical equations that can correlate and/or predict the dependence between the glass-transition temperature of a miscible system and its composition. In their chronological order, the following are the most frequently employed equations:

Gordon–Taylor equation[50]

$$T_g = \frac{w_1 T_{g_1} + k w_2 T_{g_2}}{w_1 + k w_2}$$

where T_g, T_{g_1}, and T_{g_2}, are respectively the glass-transition temperatures of the blend, of homopolymer 1, and of

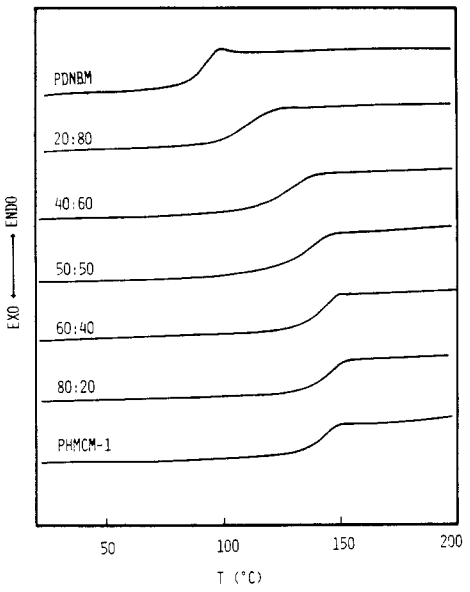


Figure 5. DSC traces of PHMCM-1–PDNBM EDA complexes of different compositions, dried at 120 °C under vacuum. (PHMCM-1/PDNBM weight ratios shown above the DSC traces.)

Table III
Glass-Transition Temperatures of Blends with PDNBM

W_2[a]	PHECM, T_g/°C	PHMCM-1, T_g/°C	PHMCM-2, T_g/°C
0.0	94	94	94
0.2	109	113	111
0.4	125	129	127
1:1[b]	132	137	125
0.6	139	143	133
0.8	144	146	136
1.0	146	144	134

[a] Weight fraction of the corresponding electron-donor homopolymers. [b] 1:1 molar ratio complex (PHECM W_2 = 0.463, PHMCM-1 W_2 = 0.463, PHMCM-2 W_2 = 0.425).

homopolymer 2, w_1 and w_2 are the corresponding weight fractions, and k is the ratio between the volume expansion coefficients of the homopolymers in the mixture.

Jenckel–Heusch equation[51]

$$T_g = w_1T_{g_1} + w_2T_{g_2} + w_1w_2b\,(T_{g_1} - T_{g_2})$$

where T_g, T_{g_1}, T_{g_2}, w_1, and w_2 have the same meaning as in the previous case, and b is an empirical parameter that varies from system to system.

Fox equation[52]

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}}$$

where T_g, T_{g1}, T_{g2}, w_1, and w_2 have the same meaning as before.

Couchman equation[53,54]

$$\ln T_g = \frac{w_1(\Delta C_{p_1}) \ln T_{g_1} + w_2(\Delta C_{p_2}) \ln T_{g_2}}{w_1(\Delta C_{p_1}) + w_2(\Delta C_{p_2})}$$

where T_g, T_{g_1}, T_{g_2}, w_1, and w_2 have the same meaning as previously discussed, while ΔC_{p_1} and ΔC_{p_2} are the changes in the heat capacity of the polymers 1 and 2 at their glass-transition temperatures.

Kwei equation[26]

$$T_g = \frac{w_1T_{g_1} + kw_2T_{g_2}}{w_1 + kw_2} + qw_1w_2$$

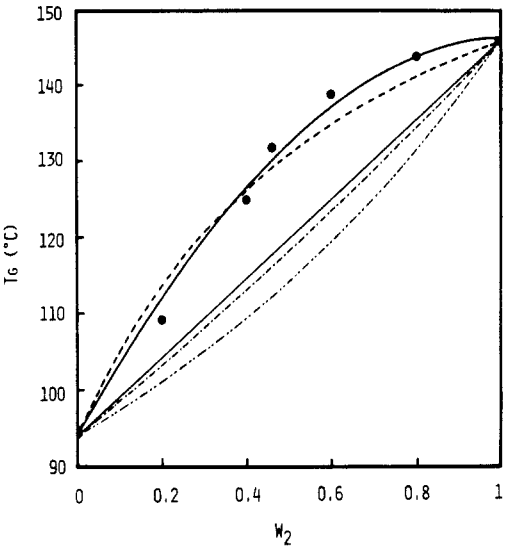


Figure 6. Glass-transition temperatures of PHECM–PDNBM EDA complexes vs. weight fraction of PHECM (W_2), and theoretical curves predicted by Kwei (—), Gordon–Taylor (---), Couchman (-·-·), and Fox (·····) equations.

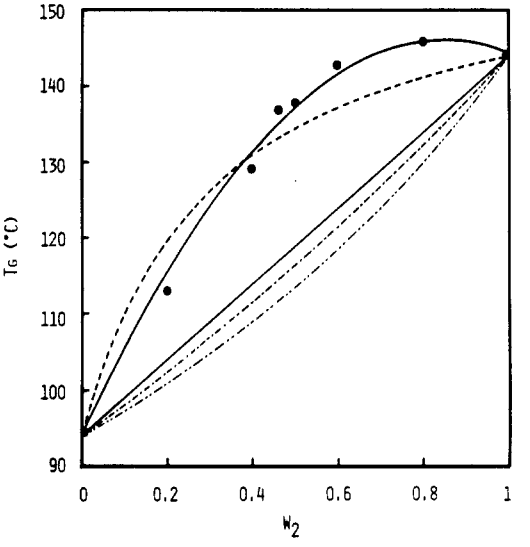


Figure 7. Glass-transition temperatures of PHMCM-1–PDNBM EDA complexes vs. weight fraction of PHMCM-1 (W_2), and theoretical curves predicted by Kwei (—), Gordon–Taylor (---), Couchman (-·-·), and Fox (·····) equations.

where T_g, T_{g_1}, T_{g_2}, w_1, w_2, and k have the same meaning as before, while the quadratic term qw_1w_2 is assumed to be proportional to the number of specific interactions between the two polymers. 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 for which $b(T_{g_1} - T_{g_2}) = q$.

Usually the k value from the Gordon–Taylor equation[55,56] and the q value from the Kwei equation[26] are used to estimate the strength of the interchain interaction. In Kwei's equation the increase in T_g due to polymer–polymer interaction is equal to the T_g increase per bond (complex) times the number of bonds, the latter being proportional to w_1w_2. Accordingly, q is equal to the increase in T_g per bond times a proportionality constant that relates the number of bonds to w_1w_2.

Figures 6 and 7 show the glass-transition temperatures of the blends of PHECM and PHMCM-1 with PDNBM, respectively, as well as the values predicted by the various equations. Couchman's equation was plotted by using the

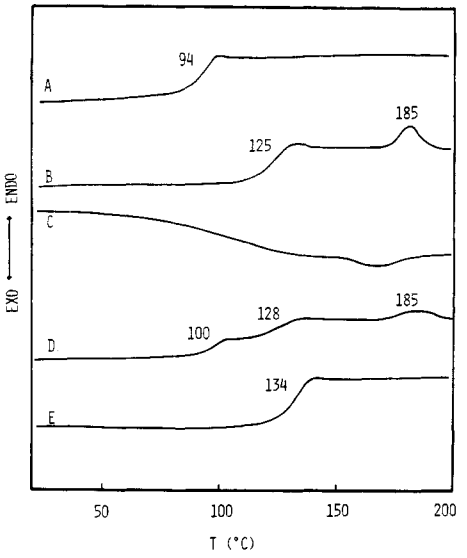


Figure 8. DSC traces of PDNBM and PHMCM-2 and their 1:1 EDA complex, dried at 120 °C under vacuum: (A) PDNBM; (B) complex, first scan; (C) complex, cooling curve; (D) complex, second scan; (E) PHMCM-2.

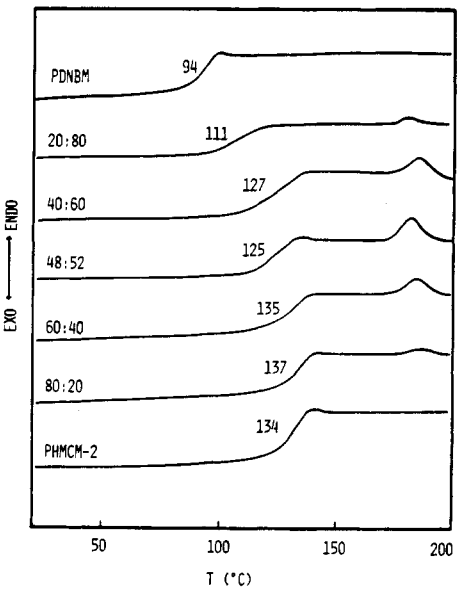


Figure 9. DSC traces of PHMCM-2–PDNBM EDA complexes of different compositions, dried at 120 °C under vacuum. (PHMCM-2/PDNBM weight ratios shown above the DSC traces.)

following heat capacity changes: ΔC_p PHECM = 0.068, ΔC_p PHMCM-1 = 0.063, and ΔC_p PDNBM = 0.072. The values of the constant parameter k in the Gordon–Taylor equation and k and q in the Kwei equation were determined by standard least-square procedures to obtain the best fit with the experimental points. As can be seen in these figures, the best fit of the experimental results is given by the equation proposed by Kwei with $k = 1$ and $q = 49.70$ for the PHECM–PDNBM system, and $k = 1$ and $q = 72.94$ for the PHMCM-1-PDNBM system. Since in both cases $k = 1$, the same fit would be obtained with the Jenckel–Heusch equation with $b = -0.96$ for PHECM–PDNBM and $b = -1.46$ for PHMCM-1–PDNBM. It is not surprising that all equations except that proposed by Kwei could not fit our data. This is because they do not take into account interchain interactions as responsible for polymer miscibility. The same is true also for Couchman's equation, which fit neither our data nor the data of some other authors'.[57] This is not unexpected since the thermodynamic standpoint of this equation is still disputed.[58]

The positive deviation of the glass-transition temperatures of both systems from the weight-average values is an indication of very strong interchain interactions which decrease the mobility of the polymer chains. In this case both systems behave as thermally reversible cross-linked networks. Both EDA complexes can be dissolved in Me_2SO above 150 °C. A further increase in the solution temperature is accompanied by a decrease in the intensity of their color. Repeated attempts to observe the decomplexation of these systems in solid state, by heating in the DSC up to their decomposition temperatures, failed to evidence any endotherm. Positive deviations of the glass-transition temperatures were previously encountered in polymer blends presenting very strong hydrogen bonding interchain interactions, and were explained on the basis of reversible cross-linking.[11,26]

Finally if the values of k from the Gordon–Taylor equation and the values of q from the Kwei equation are taken as an indicative measure of the strength of the interchain interactions, it would seem that the system PHMCM-1–PDNBM exhibits stronger interactions than the PHECM–PDNBM system.

Solid-State Characterization of PHMCM-2–PDNBM EDA Complexes. This EDA complex system was prepared from THF solutions of the two polymers. Complexes dried under vacuum at room temperature present much lower T_g values than those dried at 120 °C under vacuum. This is in agreement with the two systems discussed previously. Curves A and E in Figure 8 represent the DSC scans of the PDNBM and PHMCM-2, respectively. The first heating scan (first heating after drying at 120 °C under vacuum) of the sample PDNBM–PHMCM-2 (1:1 molar complex) is presented as curve B and the first cooling scan as curve C. It is interesting to denote a single T_g and an endotherm at 185 °C on curve B. On cooling (curve C) we see an exotherm which presents a smaller caloric effect than the endotherm on heating. It is difficult on cooling scans to read the value of T_g. The second heating scan is shown as curve D. It shows two glass transitions, both shifted in comparison to those of the parent homopolymers, and an endotherm presenting a smaller caloric effect than that of the first heating scan. After this scan, if this sample is annealed at 120 °C for 12 h, cooled, and rescanned on heating, the DSC trace is again identical with that of curve B. When the first heating scan does not reach the endotherm at 185 °C, on cooling and reheating, it continues to present a single T_g. This behavior can be explained in the following manner. Since this system presents weaker interchain interactions in comparison with the previous two systems, its solid-state decomplexation occurs below the decomposition temperature, i.e., at ~185 °C. If we cool this complex at a cooling rate that does not provide the kinetic pathway for the thermodynamic miscibility to be realized, it behaves as a two-phase system. In this case we still have very strong interchain interactions but only at the domain interface, and these are responsible for the endotherm on curve D.

It is evident that this complex can be considered as a system which is thermodynamically miscible but presents a lower critical solution temperature (LCST).[58-60] To our knowledge this is the first system presenting a LCST that can be detected by DSC. At the same time the thermodynamic parameters of this system can be determined by DSC, and some preliminary quantitative data will be discussed later.

Figure 9 shows the DSC traces of PDNBM, PHMCM-2, and a set of EDA complexes (dried at 120 °C). The com-

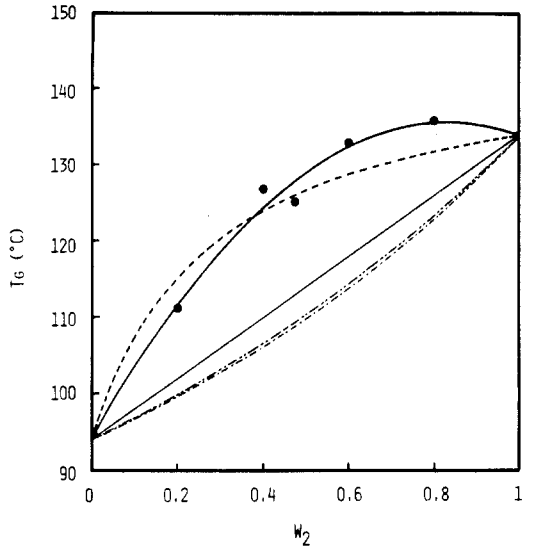


Figure 10. Glass-transition temperatures of PHMCM-2–PDNBM EDA complexes vs. weight fraction of PHMCM-2 (W_2), and theoretical curves predicted by Kwei (—), Couchman (-·-·), Fox (·····), and Gordon–Taylor (---) equations.

Table IV
Constant Parameters in the Gordon–Taylor, Kwei, and Jenckel–Heusch Equations Used to Evaluate the Miscible Systems[a]

system	Gordon–Taylor, k	Kwei k	Kwei q	Jenckel–Heusch, b
PHECM–PDNBM	2.48	1.0	49.70	−0.96
PHMCM-1–PDNBM	4.26	1.0	72.94	−1.46
PHMCM-2–PDNBM	4.51	1.0	59.99	−1.50

[a] Calculated by least squares to obtain the best fit of experimental data.

position of these complexes is presented on their scans. We can see that the two polymers are miscible over the entire range of composition. At the same time all the DSC traces exhibit an endotherm whose caloric effect depends on the EDA complex composition. The largest endotherm obviously occurs for the 1:1 EDA complex. In all cases, when the complexes are heated to temperatures below this endotherm and cooled, all the DSC scans are reproducible and present only a single T_g.

The dependence between the T_g of the miscible system and EDA complex composition is presented in Figure 10. This data is also presented in Table IV. Again a positive deviation of the T_g values from that of the weight average of the parent polymers is observed. The estimation of this system by the Gordon–Taylor (k = 4.51), Fox, Couchman (ΔC_p PDNBM = 0.072, ΔC_p PHMCM-2 = 0.050), and Kwei (k = 1.0006, q = 59.65) equations is also shown in the figure. It is obvious that again the Kwei equation is the best to describe this system. As the k value in Kwei's equation is equal to 1, this system can be well described also by the Jenckel–Heusch equation (b = −1.50).

The values of k and q of the Kwei equation and k of Gordon–Taylor equation characterizing all three systems studied are summarized in Table IV. Obviously, the trend of k values from the Gordon–Taylor equation does not follow the real strength of the interchain interactions. According to this data, the system PHMCM-2–PDNBM presents stronger interchain interactions than the other two systems. The real situation is just the opposite. We wonder if the values of k obtained from the Gordon–Taylor equation for different systems and used in the literature to judge the strength of interchain intractions do indeed have any physical meaning. Further comments on this subject will be made later. The values of q from the Kwei equation follow the expected trend for the systems based on PHMCM-1 and PHMCM-2, but the system based on PHECM has a lower q value than expected. The enthalpy changes associated with the decomplexation endotherm at 185 °C for both the miscible systems (first heating scan, for an example see curve B in Figure 8 and DSC traces in Figure 9), and for the immiscible systems (second heating scan, for an example see curve D in Figure 8) were quantitatively evaluated. A set of samples containing larger amounts of EDA complex than those used for the evaluation of the glass-transition temperatures were run at different sensitivities of the DSC instrument, and the enthalpy changes were calculated by using In as standard. The enthalpy changes associated with the first heating scan and the difference between the first scan and the average of the second and third scans are summarized in Tables V and VI. As we have discussed before, the enthalpy change associated with the first scan is assumed to be equal to the enthalpy of decomplexation of the EDA complex. The second scan gives the enthalpy of complexation at the interphase of the two domains present in the phase-separated system. The difference between the enthalpy change associated with the decomplexation of a one-phase system and the enthalpy change associated with the decomplexation of the two-phase system should account for the enthalpy change required to transform the phase-separated system into a miscible system. Table V presents these values reported in grams of polymer mixture, while Table VI presents the same data reported in moles of 1:1 D–A pairs in the EDA complex. The 1:1 composition of an EDA complex is still disputed,[2,61] and the real one might be either 2D:1A or 2A:1D. Because at this time we do not have the equilibrium constant for this EDA complex (this would let us estimate the numbers of D and A groups complexing), the discussion that follows is only qualitative.

Figure 11 shows a plot of the data from Table V as a function of the polymer mixture composition. The highest

Table V
Enthalpy Change of the Endotherm at 185 °C in the PHMCM-2–PDNBM Complexes

W_2[a]	ΔH/(cal·g^{-1}) scan 1[b]	scan 2[c]	scan 3[c]	$\Delta\Delta H$/(cal·g^{-1})[d]
0.2	0.45	0.24	0.21	0.23
0.4	0.52	0.34	0.37	0.14
0.475[e]	0.68	0.34	0.33	0.35
0.6	0.53	0.43	0.38	0.13
0.8	0.43	0.27	0.29	0.15

[a] Weight fraction of PHMCM-2. [b] Heating scan after drying at 120 °C under vacuum for 12 h. [c] Heating scan after quenching at 320 °C/min to 0 °C. [d] Difference between first scan and the average of the second and third scans. [e] 1:1 molar ratio.

Table VI
Enthalpy Change of the Endotherm at 185 °C in the PHMCM-2–PDNBM System[a]

W_2[b]	ΔH/(cal·mol^{-1}) scan 1[c]	scan 2[d]	scan 3[d]	$\Delta\Delta H$/(cal·mol^{-1})[e]
0.2	660.8	352.0	308.8	330.4
0.4	382.9	384.1	271.7	105.0
0.475[f]	419.9	210.0	210.0	209.9
0.6	426.2	345.9	308.8	116.9
0.8	697.9	438.5	469.9	244.0

[a] Cal/mol of 1:1 D–A structural unit pairs present in the blend. [b] Weight fraction of PHMCM-2. [c] Heating scan after drying at 120 °C under vacuum for 12 h. [d] Heating scan after quenching at 320 °C/min to 0 °C. [e] Difference between first scan and the average of the second and third scans. [f] 1:1 molar ratio.

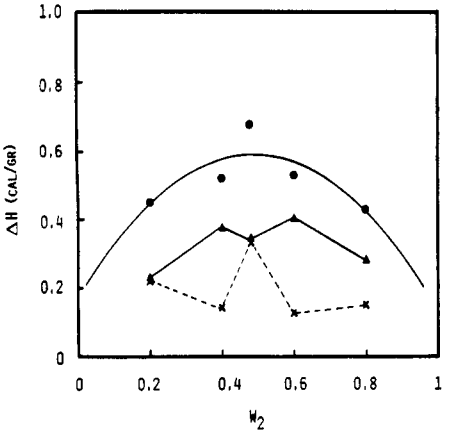


Figure 11. ΔH (cal/g of polymer mixture) of the endotherm at 185 °C of PHMCM-2–PDNBM complexes as a function of weight fraction of PHMCM-2 (W_2): (●) first scan; (▲) average of second and third scans; (x) difference between the first scan and the average of the second and third scans.

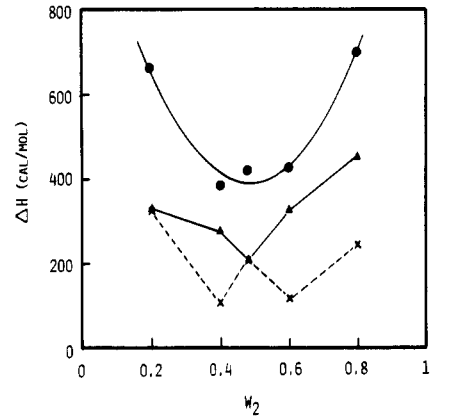


Figure 12. ΔH of the endotherm at 185 °C of PHMCM-2–PDNBM complexes as a function of weight fraction of PHMCM-2 (W_2), in cal/mol of 1:1 D–A structural unit pairs in the mixture assuming 1:1 stoichiometry of the complex: (●) first scan; (▲) average of second and third scans; (x) difference.

enthalpy change in the first heating scan occurs as expected for a 1:1 molar ratio between the two polymers. The other data are perfectly symmetrical. The same excess of D or A groups gives the same enthalpy change, since there is the same concentration of D–A interaction groups in both cases. The enthalpy change associated with the interaction at the interface should be dependent on the morphology of the phase-separated system which will dictate the area of the interface. We do not yet have morphological studies available. In any case the enthalpy change associated with the complexation at the interface is not maximum for a 1:1 ratio of the two polymers but for the two compositions around it. This is certainly due to the difference in the interface area for these systems. On this account the enthalpy change required to transform the immiscible system into a miscible one is maximum for a 1:1 ratio of the two polymers in the blend, it then drops and increases again toward the low concentrations of either one of the polymers in the mixture.

Figure 12 shows a different point of view. Here the enthalpy changes are plotted as moles of 1:1 D–A pairs (data from Table VII). The enthalpy change in the first heating scan is maximum at the two extremes of the EDA complex compositions. This clearly demonstrates that the maximum number of D–A groups interacting (from the total number of D–A groups present in the system) appears for compositions containing large excess of either D or A groups. This is an important conclusion since it demonstrates what an equilibrium process depicted by the equation $k = [DA]/[D][A]$ (where k is the equilibrium constant, [DA] is the concentration of the EDA complex, and [A] and [D] are the concentrations of A and D, respectively) predicts. This supports the conclusion that the endothermal processes are indeed due to the decomplexation of the EDA complexes. The plots of the enthalpy changes from the second DSC scans and of the difference of the first and second DSC scans obey the expected behavior. A quantitative study of this system is in progress and will be reported soon.

Table VII
Glass-Transition Temperatures of PHMCM-*n*-PDNBM Complexes[a]

PHMCM-*n*, *n*	scan 1,[b] T_g/°C	scan 2,[c] T_g/°C	after drying[d] T_g/°C
4	65	98	102
6	61	92, 38	100, 65
8	48	85, 26	101, 57
10	38	87, 20	101, 41
12	37	86, 20	101, 29
14	35	84, 19	100, 27
16	34	86, 18	100, 27

[a] Complexes prepared from THF solution. [b] Heating scan after drying at room temperature under vacuum for 24 h. [c] Heating scan after quenching at 320 °C/min to 0 °C. [d] Heating scan after drying at 100 °C under vacuum for 12 h.

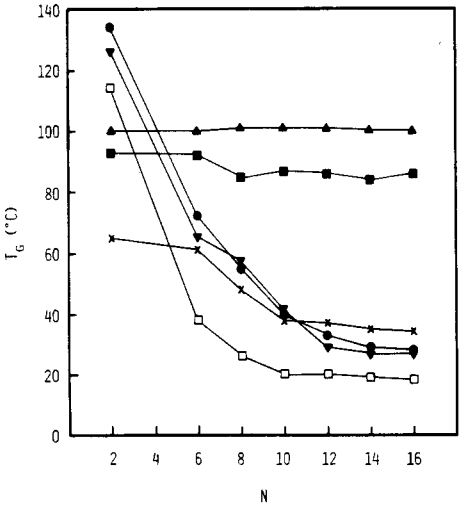


Figure 13. Glass-transition temperatures of PHMCM-*n* and their EDA complexes with PDNBM (as obtained from solution, dried at room temperature under vacuum for 24 h): (●) PHMCM-*n*; (x) complexes, first scan; (■) complexes, upper T_g, second scan; (□) complexes, lower T_g, second scan; (▲) complexes, upper T_g, after drying at 120 °C under vacuum for 12 h; (▼) complexes, lower T_g, after drying at 120 °C under vacuum for 12 h.

Solid-State Characterization of the PHMCM-*n*–PDNBM EDA Complexes ($n > 2$). The EDA complexes of PHMCM-*n*–PDNBM containing more than two carbon atoms in the side chain were studied only at 1:1 molar ratio. All the room temperature dried complexes show a single T_g on the first heating scan. The second heating scan did present two T_g's in all cases except for PHMCM-4–PDNBM. In this case both homopolymers have almost the same glass-transition temperature (93 and 94 °C, respectively) and it is impossible to discriminate between the miscible and phase-separated systems. No endotherms could be detected on their DSC traces. These experimental data are summarized in Table VII and plotted in Figure 13. Apparently all these systems are thermodynamically miscible but present a LCST. These systems behave the same way as most of the classical systems presenting LCST

available in the literature. The LCST could not be detected by DSC measurements since the decomplexation endotherm is not visible, possibly due to the very weak interchain interactions. The glass-transition temperatures of the complexes free of THF are shifted in comparison with those of the parent homopolymers. This can be explained through the presence of a weak interaction at the interface. The shift in the T_g value decreases with the increase of the number of carbons in the groups and is completely absent in the system PHMCM-16–PDNBM. This means that this system could meet the requirements of the first goal of this research.

Conclusions

Interchain EDA interactions can be used as a model system to induce and study polymer miscibility. In the case of the interchain EDA complexes PHMCM-*n*–PDNBM the strength of the interactions can be easily controlled by varying the length of the alkyl side chain. Three types of behavior are observed. First, complexes of polymers with short or no alkyl side chains like PHMCM-1 and PHECM produce blends that are miscible over all the concentration ranges studied, and no phase separation occurs even when they are heated to their decomposition temperatures. Second, the EDA complexes of PHMCM-2, which are miscible at temperatures below 185 °C, show a "decomplexation" endotherm at this temperature. This system could be considered as showing LCST and is the first available model on which thermodynamic parameters could be determined by DSC. Third, complexes of polymers with $n > 4$ are apparently thermodynamically miscible but present a LCST that cannot be detected by DSC.

Finally, of all the equations available in the literature relating the glass-transition temperatures of polymer blends with those of the parent homopolymers and their composition, only the one recently proposed by Kwei[26] best describes the behavior of these miscible systems. The glass-transition temperatures of the systems PHECM–PDNBM, PHMCM-1–PDNBM, and PHMCM-2–PDNBM present large positive deviations from the weight-average values. This is evidence for the formation of thermal reversible cross-linked networks through interchain EDA complexes.

Acknowledgment. We wish to acknowledge the financial support of the National Science Foundation Polymers Program under Grant No. DMR-82-13895, as well as that of a NATO traveling grant. Gratitude is also extended to Professors H. J. Cantow, J. M. Cowie, and R. Simha for their helpful discussions.

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