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Compatible Blends

Interchain EDA Complexes of Poly[N-(2-Hydroxyethyl) Carbazolyl Methacrylate] with Poly (ω-Hydroxyalkyl-3,5-Dinitrobenzoyl Methacrylate)s

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SUMMARY

The solid state behavior of the interchain electron donor-acceptor (EDA) complexes of poly[N-(2-hydroxyethyl)carbazolyl methacrylate] (PHECM) with poly(ω-hydroxyalkyl-3,5-dinitrobenzoyl methacrylate)s (PDNBM-n) (where n is the number of methylene groups in the hydroxyalkyl group) with n=2, 3, 4, 5 and 6 was studied by differential scanning calorimetry. All these systems form thermodynamically miscible blends. The dependence of the glass transition temperature (T_g) on the blend composition can be best aproximated by the Kwei's equation.

INTRODUCTION

It has been demonstrated that interchain electron donor-acceptor (EDA) interactions can be used to induce polymer-polymer miscibility, and that miscibility can be controlled through the strength and number of donor-acceptor (DA) interactions (1-6).

Recently, we have classified miscibility induced by EDA interchain complexes in two classes. The first one refers to interchain EDA complexes which are thermodynamically miscible and in which the miscibility is thermodynamically controlled (3, 4, 6). In these systems, the solid-state decomplexation does not occur below the decomposition temperature of the polymer blend. The second class refers to interchain EDA complexes which are thermodynamically miscible but in which the miscibility is kinetically controlled (3, 5, 6). In these interchain EDA complexes the solid-state decomplexation does occur below the decomposition temperature of the complex. It appears as an endotherm on the differential scanning calorimetric curves, and has a similar meaning as the lower crytical solution temperature (LCST). Depending on the kinetic treatment of these complexes they can form either a miscible blend or a phase separated system. In the last case, the decomplexation endotherm is due to the interchain EDA interactions at the interface. Therefore, the second class of EDA complexes has provided the first available polymer systems on which basic thermodynamic parameters could be determined by DSC (3, 5, 6).

On this account we are interested in understanding the structural particularities of interchain EDA complexes which lead to either thermodynamically or kinetically controlled miscible systems. The goal of this paper is to present our data on the interchain EDA complexes of poly[N-(2-hydroxyethyl) carbazolyl methacrylate] (PHECM) with poly(ω-hydroxyalkyl-3,5-dinitrobenzoyl methacrylate)s (PDNBM-n) (where n is the number of methylene groups in the hydroxyalkyl group) with n=2, 3, 4, 5 and 6.

EXPERIMENTAL

Synthesis of PHECM and PDNBM-n (n=2, 3, 4, 5 and 6)

HECM (7) and DNBM-n (5,8) were synthesised as was previously reported. PHECM and PDNBM-n were obtained by radical polymerization of the corresponding monomers (AIBN = 2 weight% from the monomer) in dioxane under argon atmosphere at 60°C for 15 hrs. Monomer concentrations were 25% for DNBM-n and 10% for HECM. All polymers were purified by precipitation into methanol from THF solutions.

Preparation of the Interchain EDA Complexes

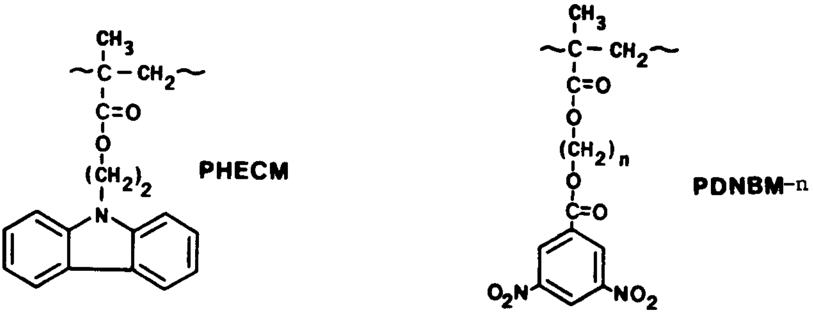
Interchain EDA complexes were prepared by mixing THF solutions of the D and A containing polymers, followed by slow evaporation of the solvent at room temperature and then vacuum drying at 120°C to constant weight.

Techniques

Glass transition temperatures (T_g) 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 T_g values were read during the second heating cycle. Molecular weights were determined by gel permeation chromatography (GPC), in a Perkin-Elmer series 10LC equiped 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), and a set of PL-gel columns of 10^2, 5×10^2, 10^3, 10^4 and 10^5Å, and a calibration plot constructed with polystyrene standards.

RESULTS AND DISCUSSION

Scheme 1 presents the structure of the D and A polymers. The molecular weights and T_g values of the D and A polymers are presented in Table 1.



Scheme 1: Structure of Donor and Acceptor Polymers

Table 1: Characterization of Donor and Acceptor Polymers

Polymer	$\bar{M}n \times 10^{-4}$	$\bar{M}w \times 10^{-4}$	$\bar{M}w/\bar{M}n$	T_g (°C)
PHECM	3.1	14.2	4.5	146
PDNBM-2	2.42	10.24	4.21	94
PDNBM-3	1.83	2.76	1.51	72
PDNBM-4	1.93	5.43	2.81	57
PDNBM-5	1.99	3.90	1.96	33
PDNBM-6	2.04	3.60	1.77	23

Previously we have shown that within this range of molecular weights both the T_g of the homopolymers and of their interchain EDA complexes are not molecular weight dependent (3, 6). We have also demonstrated that the system PHECM-PDNBM-2 is thermodynamically miscible, that the miscibility is thermodynamically controlled, and that this behavior does not depend on the molecular weight of the PHECM (3, 6). Interchain EDA complexes with lower T_g than the system PHECM-PDNBM-2 are of particular interest for rheological studies (1, 2). Such a system can be obtained by decreasing the T_g value of one of the two polymers i.e., by increasing the length of the spacer between the donor or acceptor group and the polymer chain. Therefore, it is important to understand how the length of the spacer between the acceptor group and the polymer chain would affect the miscibility behavior of the interchain complex. Table 2 presents the T_g values of the PHECM-PDNBM-n interchain EDA complexes.

Table 2: Glass Transition Temperatures of PHECM-PDNBM-n EDA Complexes

W_{PHECM} a)	PDNBM-2	PDNBM-3	PDNBM-4	PDNBM-5	PDNBM-6
			T_g in ^oC		
0.0	94	72	57	33	23
0.2	109	91	75	58	56
0.3	120	100	91	83	81
0.4	125	119	107	97	93
1:1 b)	132	122	111	106	97
0.6	139	131	126	119	115
0.8	144	139	137	134	131
1.0	146	146	146	146	146

a) W_{PHECM} = weight fraction of PHECM in EDA complex; b)1:1 molar ratio complex

All systems show a single glass transition temperature both on heating and cooling indifferent of the thermal history of the polymer sample. This demonstrates that the increase of the spacer length in the acceptor polymer from two to six methylene groups does not change the behavior of the complex i.e., it does not change it from a system where miscibility is thermodynamically controlled to one where it is kinetically controlled. This is an important conclussion which supports the idea that kinetically controlled systems can apparently be realized only when steric hyndrances affect the interchain complexation (3, 5, 6).

The dependence between the EDA complex composition and its T_g for the systems PHECM-PDNBM-n is presented in Figures 1-5. This relationship has been estimated by a variety of equations available in the literature. As it has been previously shown (3, 4) only Kwei's equation (9) can fit these data. The best fit after Kwei's equation is provided in this case by Gordon-Taylor equation (10).

Kwei equation: $T_g = (W_1T_{g1} + kW_2T_{g2})/(W_1 + kW_2) + qW_1W_2$, where: T_g, T_{g1}, and T_{g2} are , respectively, the glass transition temperature of the blend, of homopolymer 1, and of homopolymer 2, W_1 and W_2 are the corresponding weight fractions, k is the ratio between the volume expansion coefficients of the homopolymers in the mixture, while the quadratic term qW_1W_2 is assumed to be proportional to the number of specific interactions in between the two polymers. In this equation, the increase in T_g due to polymer-polymer interactions 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 which relates the number of bonds to W_1W_2.

Gordon-Taylor equation: $T_g = (W_1T_{g1} + kW_2T_{g2})/(W_1 + W_2)$, where: T_g, T_{g1}, T_{g2}, W_1, W_2 and k have the same meaning as in the previous equation.

Usually, the k value from the Gordon-Taylor equation and the q value

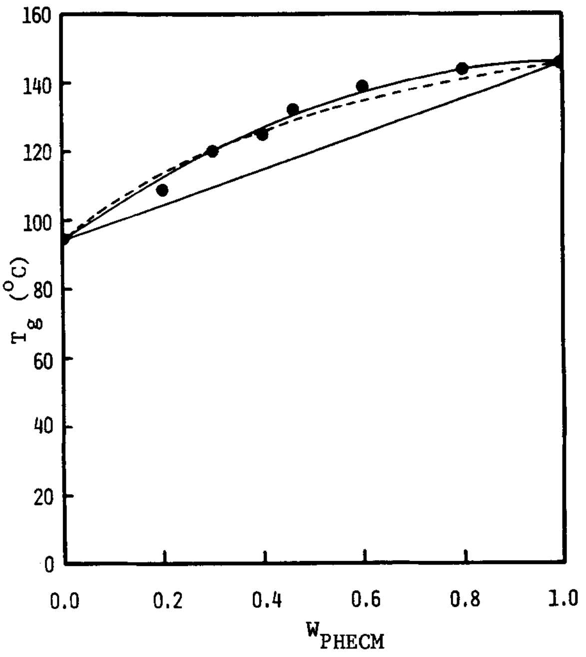


Figure 1: Glass transition temperatures of PHECM-PDNBM-2 EDA complexes vs weight fraction of PHECM, and theoretical curves predicted by Kwei (——) and Gordon-Taylor (- - -) equations

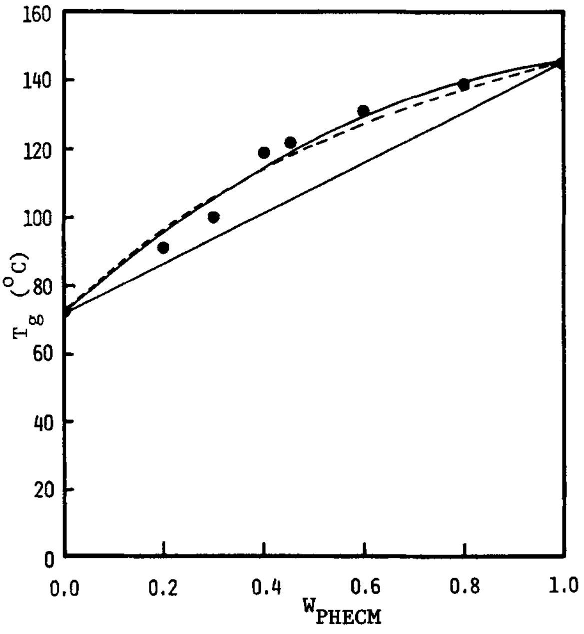


Figure 2: Glass transition temperatures of PHECM-PDNBM-3 EDA complexes vs weight fraction of PHECM, and theoretical curves predicted by Kwei (——) and Gordon-Taylor (- - -) equations

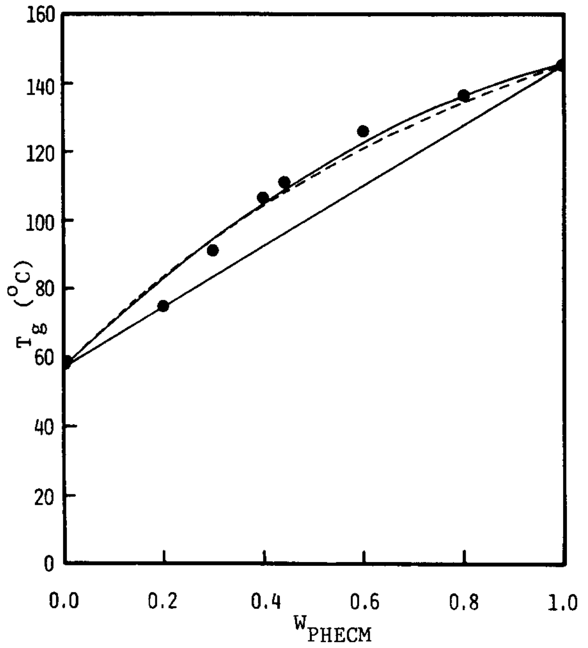


Figure 3: Glass Transition temperatures of PHECM-PDNBM-4 EDA complexes vs weight fraction of PHECM, and theoretical curves predicted by Kwei (——) and Gordon-Taylor (- - -) equations

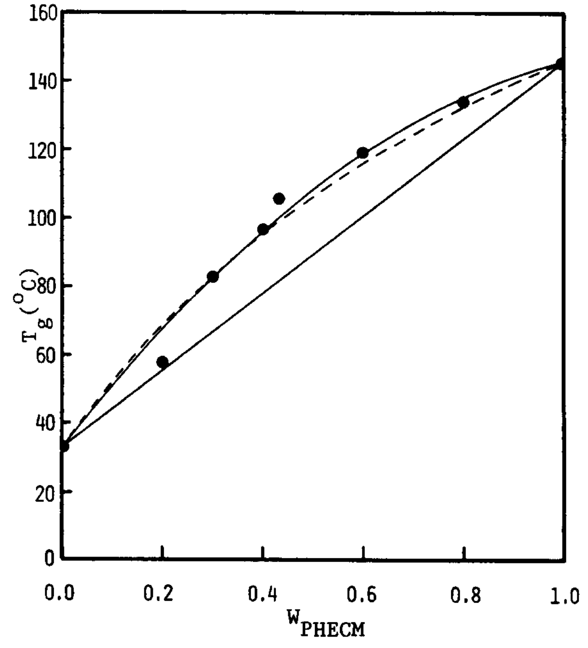


Figure 4: Glass transition temperatures of PHECM-PDNBM-5 EDA complexes vs weight fraction of PHECM, and theoretical curves predicted by Kwei (——) and Gordon-Taylor (- - -) equations

Figure 5: Glass transition temperatures of PHECM-PDNBM-6 EDA complex vs weight fraction of PHECM, and theoretical curves predicted by Kwei (——) and Gordon-Taylor (- - -) equations

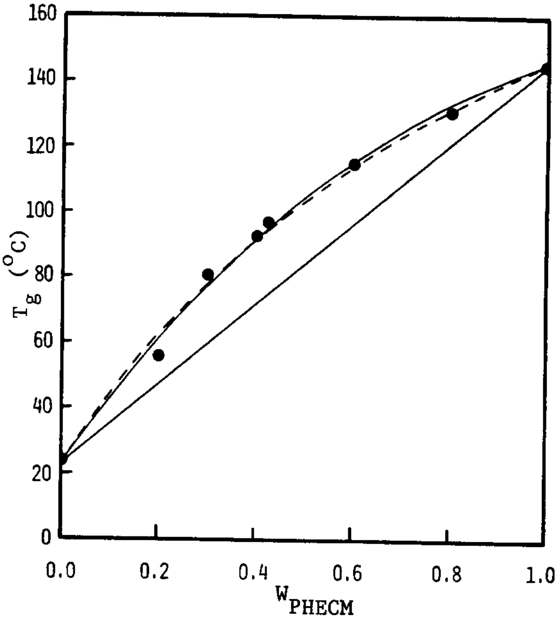
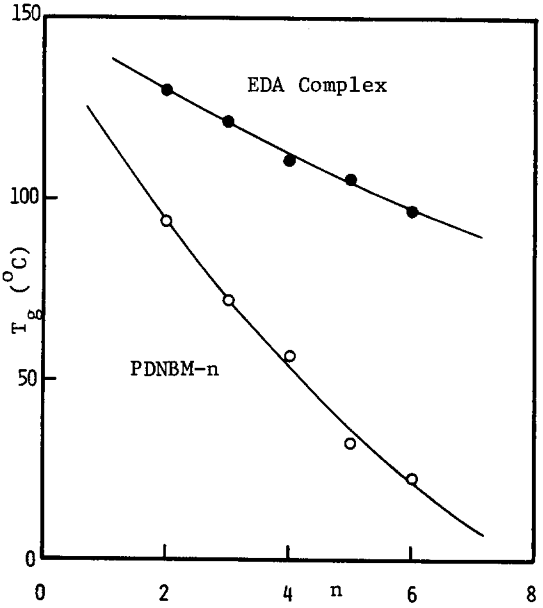


Figure 6: Glass transition temperatures of PDNBM-n (o) and their 1:1 molar complexes with PHECM (•) vs the number of methylene units "n" in the side chain of PDNBM-n



from the Kwei equation are used to estimate the strength of the interchain interaction. The values of the constant parameter k in Gordon-Taylor equation and k and q in Kwei equation were determined by standard least-square procedures to obtain the best fit with the experimental points. Table 3 presents the values of the k obtained from Gordon-Taylor equation and k and q from Kwei's equation.

Table 3: Constant Parameters in the Gordon-Taylor and Kwei equations Used to Evaluate the Glass Transition Temperatures of PHECM-PDNBM-n EDA Complexes

PDNBM-n	Gordon-Taylor	Kwei	
n	k	k	q
2	2.5	1	50
3	2.0	1	55
4	1.7	1	51
5	1.9	1	75
6	1.9	1.5	30

As in the previous cases (3, 4) the estimation of the strength of the interchain interactions by these two equations gives contradictory results. This seems to be due to the fact that these parameters can not distinguish between the number of the interacting groups and the strength of the nonbonding interaction. Further research is required to provide these quantitative data in order to develop an equation based on them.

Figure 6 presents the dependence between the T_g of PDNBM-n and of their interchain EDA complexes with PHECM, all having a 1:1 mole ratio composition. It demonstrates that indeed the T_g of these thermal reversible networks can be easily controlled by the above presented approach over a large range of temperatures.

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REFERENCES

1. H. A. Schneider, H. J. Cantow and V. Percec, Polym. Bull., 6, 617(1982)
2. H. A. Schneider, H. J. Cantow, P. Lutz and H. Northfleet-Neto, Makromol. Chem. Suppl., 8, 89(1984)
3. J. M. Rodriguez-Parada and V. Percec, Macromolecules, in press
4. C. Pugh and V. Percec, Macromolecules, in press
5. J. M. Rodriguez-Parada and V. Percec, J. Polym. Sci. Polym. Chem. Ed., in press
6. C. Pugh, J. M. Rodriguez-Parada and V. Percec, J. Polym. Sci. Polym. Chem. Ed., submitted
7. C. I. Simionescu, V. Percec and A. Natansohn, Polymer, 21, 417(1980)
8. C. I. Simionescu, V. Percec and A. Natansohn, Polym. Bull., 3, 535(1980)
9. T. K. Kwei, J. Polym. Sci. Polym. Lett. Ed., 22, 307(1984)
10. M. Gordon and J. S. Taylor, J. Appl. Chem., 2, 495(1952)

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