3394 *Macromolecules* **1998,** *31,* 3394−3396

Ramifications of Chain Connectivity in Hydrogen-Bonded Polymer Solutions

Yuhong Hu, Paul C. Painter, and Michael M. Coleman*

Department of Materials Science and Engineering,
The Pennsylvania State University,
University Park, Pennsylvania 19802

Robert J. Butera

Marshall R&D Laboratory, E. I. du Pont de Nemours & Co.,
Philadelphia, Pennsylvania 19146

Received February 18, 1998
Revised Manuscript Received April 6, 1998

In recently published work we have focused our attention on chain connectivity and its effect on the free energy of mixing and phase behavior of (co)polymer blends.[1−5] Intramolecular screening and problems pertaining to the accessibility of functional groups—factors that are a direct consequence of chain connectivity—have gone a long way to explain why the number of intermolecular hydrogen bonds formed between complementary donor and acceptor groups in single phase (miscible) (co)polymer blends is significantly less than in comparable (co)polymer solutions or mixtures of low molecular weight analogues.[6] The question we address here is as follows: Are these chain connectivity effects also important in concentrated hydrogen-bonded polymer solutions?

In this communication we present the results obtained from a series of (co)polymers containing ester or acetoxy carbonyl groups in concentrated 4-ethylphenol (EPh) solutions [i.e., those having volume fractions of the (co)polymer, Φ_A, in the range 0.25−0.65]. EPh, which was purchased from Aldrich, is a strongly self-associating (hydrogen-bonded) solid at ambient temperature with a melting point of 44 °C and a boiling point of 219 °C. Polymers used in this study, poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(*n*-butyl methacrylate) (PBMA), poly(*n*-hexyl methacrylate) (PHMA), poly(*n*-decyl methacrylate) (PDMA), poly(n-lauryl methacrylate) (PLMA), poly(vinyl acetate) (PVAc), ethylene-*stat*-vinyl acetate (EVA) copolymers containing 70, 45 and 40 wt % VAc, denoted EVA[70] etc., and ethylene-*stat*-methyl methacrylate (EMMA) copolymers containing 47, 38, and 33 wt % MMA, denoted EMMA[47] etc., have been described in previous studies.[2] 2,3-Dimethylbutadiene-*stat*-methyl methacrylate (DMBMMA) copolymers containing 70 and 51 wt % MMA, denoted DMBMMA[70] etc. were synthesized by Dr. G. Pehlert and are described in his Ph.D. thesis.[7]

Polymer solutions were prepared by initially dissolving known weights of the (co)polymers in a large excess of EPh and stirring in sealed vials at 50 °C for 48 h. A portion of the EPh was then removed under reduced pressure to yield concentrated solutions of known compositions (in the range $\Phi_A = 0.25-0.65$). All the polymer solutions considered in this communication were deemed single phase (miscible) as they were optically clear at ambient temperature and exhibited unequivocal single T_g's in a range from −22 to −72 °C [depending on the concentration and specific (co)polymer under consideration].[8] The concentrated polymer solutions were quickly "smeared" between two KBr windows, and then Teflon tape was wrapped around the edges of the windows to reduce the possibility of significant evaporation of EPh. This procedure was tested and found to be remarkably reproduceable (which is perhaps not so surprising given the relatively high boiling point of EPh, 219 °C). Measurements of the fraction of hydrogen bonded carbonyl groups, $f_{HB}^{C=O}$, using infrared spectroscopy on replicate samples of the concentrated solutions over periods of up to at least 6 h were reproduceable and were well within the normal error encountered for nonvolatile polymer blend samples. Infrared spectroscopic measurements were recorded on a Digilab model FTS45 Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. Special attention was paid to ensure that all the samples examined were sufficiently thin to be within the absorption range where the Beer−Lambert law is obeyed. Thermal analysis was conducted on a Seiko Instruments differential scanning calorimeter (DSC-220CU) coupled to a computerized data station. A heating rate of 20 °C/min. was used and the glass transition temperatures recorded as the midpoint of the heat capacity change.

Table 1. Data for Concentrated EPh Solutions of Vinyl Acetate Copolymers

(co)polymer	vol frn EPh Φ_B	$f_{HB}^{C=O}$	V_A, cm^3/mol	no. of carbons[a] between funct grps	K_A^{STD}
PVAc	0.758	0.64_4	69.8	1	110
	0.669	0.59_5			
	0.589	0.52_2			
	0.568	0.49_2			
EVA[70]	0.726	0.75_0	113	3.6	153
	0.639	0.70_5			
	0.526	0.61_6			
	0.584	0.54_7			
EVA[45]	0.721	0.82_9	194	8.5	163
	0.587	0.75_4			
	0.507	0.70_4			
	0.408	0.62_7			
EVA[40]	0.710	0.81_1	222	10.2	164
	0.594	0.77_7			
	0.521	0.74_5			
	0.413	0.64_3			

[a] Average number of backbone carbons between functional groups in specific repeat—see text.

The experimental methodology for the determination of the $f_{HB}^{C=O}$ from concentrated EPh solutions of the (co)polymers using infrared spectroscopy, including the use of simulations to establish the range of compositions over which measurements can be most accurately performed, has been described fully in refs 1, 2, 3, and 6, and will not be restated here (raw data are available on request from the authors).[8] In Tables 1−3 we summarize the $f_{HB}^{C=O}$ data obtained from EPh solutions of known volume fraction (Φ_B) for a series of vinyl acetate (co)polymers, methyl methacrylate (co)polymers and poly(*n*-alkyl methacrylate) homopolymers, respectively. It is convenient to compare the $f_{HB}^{C=O}$ formed in single phase polymer blends or solutions, by equating the magnitude (in dimensionless units) of standard interassociation equilibrium constants, K_A^{STD}, that have been scaled to a common reference molar volume of 100 cm^3/mole at 25 °C.[1,2,3,6] K_A^{STD} values shown in the final columns were determined from a least-squares fit of the $f_{HB}^{C=O}$ data to the appropriate stoichiometric

S0024-9297(98)00248-4 CCC: $15.00

Table 2. Data for Concentrated EPh Solutions of Methyl Methacrylate Copolymers

(co)polymer	vol frn EPh Φ_B	$f_{HB}^{C=O}$	V_A, cm^3/mol	no. of carbons[a] between funct grps	K_A^{STD}
EMMA[47]	0.709	0.82_3	218	9.1	163
	0.606	0.77_6			
	0.493	0.71_7			
EMMA[38]	0.706	0.83_6	277	12.6	166
	0.611	0.80_1			
	0.525	0.76_5			
	0.409	0.71_2			
EMMA[33]	0.577	0.79_7	324	15.5	164
	0.508	0.77_6			
	0.462	0.75_7			
DMBMMA[70]	0.650	0.70_9	133	3.1	156
	0.530	0.65_2			
	0.451	0.58_9			
DMBMMA[51]	0.630	0.75_8	193	5.7	165
	0.544	0.72_9			
	0.468	0.68_7			
	0.356	0.61_0			

[a] Average number of backbone carbons between functional groups in specific repeat—see text.

Table 3. Data for Concentrated EPh Solutions of Poly(*n*-Alkyl Methacrylate) Polymers

polymer	vol frn EPh Φ_B	$f_{HB}^{C=O}$	V_A, cm^3/mol	no. of carbons[a] between funct grps	K_A^{STD}
PMMA	0.738	0.65_0	84.9	1	101
	0.664	0.60_7			
	0.560	0.52_2			
	0.471	0.43_5			
PEMA	0.721	0.65_2	101	1	95
	0.605	0.57_7			
	0.543	0.53_1			
	0.449	0.45_8			
PBMA	0.706	0.65_0	134	1	88
	0.622	0.62_6			
	0.517	0.57_2			
PHMA	0.689	0.64_0	167	1	73
	0.622	0.62_7			
	0.490	0.54_6			
	0.414	0.47_1			
PDMA	0.700	0.65_5	233	1	75
	0.613	0.63_9			
	0.522	0.61_9			
	0.383	0.52_3			
PLMA	0.678	0.64_4	266	1	73
	0.556	0.63_2			
	0.509	0.61_7			
	0.445	0.60_7			

[a] Average number of backbone carbons between functional groups in specific repeat—see text.

equations, a now routine process that again has been described previously in detail.[1,2] Necessary parameters include the molar volume of EPh, $V_B = 130$ cm^3/mol, the corresponding values of the EPh self-association equilibrium constants at 25 °C, $K_2 = 16.2$ and $K_B = 51.4$ dimensionless units,[6] and the molar volumes of the average specific repeat of the different (co)polymers, V_A, which are estimated from group contributions[1] and given in Tables 1−3.

In common with the trends observed for miscible DMBVPh blends with EVA and EMMA copolymers,[2,3] the K_A^{STD} results presented in Tables 1 and 2 demonstrate that the "spacing" effect also occurs in concentrated EPh solutions. For example, increasing values of $K_A^{STD} = 110$, 153, 163, and 164 dimensionless units were determined for concentrated EPh solutions of PVAc, EVA[70], EVA[45] and EVA[40], while a similar trend, i.e., $K_A^{STD} = 101$, 163, 166, and 164 dimensionless units, was observed for PMMA, EMMA[47], EMMA[38], and EMMA[33]. Moreover, from Table 3, for the series of poly(*n*-alkyl methacrylates) (PAMA) the K_A^{STD} values decrease from 101 for PMMA to 95 for PEMA to 88 for PBMA and finally level off at ≈74 dimensionless units for PHMA and the higher homologues. A similar trend was observed for PAMA blends with a DMBVPh[24] copolymer[2] and was attributed to an increased steric shielding of the carbonyl groups with increasing size of the side groups.

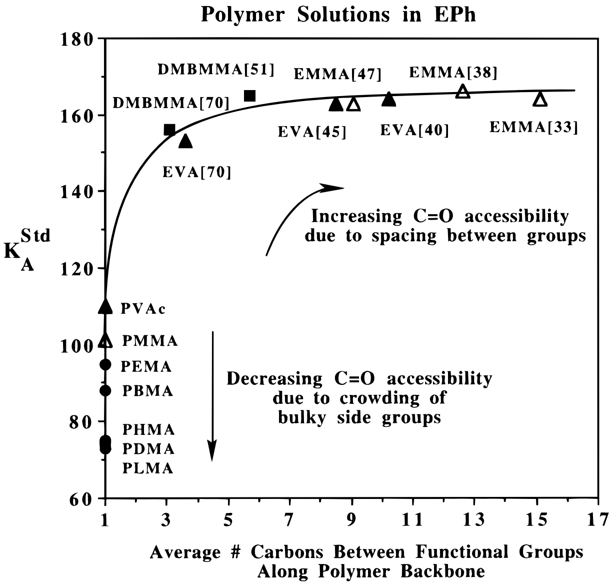
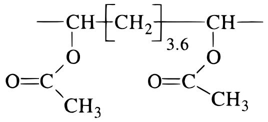


Figure 1. Plot of vs the average number of backbone carbons between functional groups for concentrated solutions in EPh.

In Figure 1 we present a graph of K_A^{STD} values plotted against the average number of backbone carbons between functional groups in the "specific" repeat unit, which is a rough measure of the average distance between functional groups. As this is a somewhat different format to that used previously,[2,3] we feel it is necessary to elaborate. Using EVA[70] as an example



EVA[70]

the number of backbone carbons (methylene units) between >CH−OAc groups in an average repeat of the copolymer backbone is 3.6. The corresponding values for the other copolymers are included in the fifth column of Tables 1 and 2. [In the case of the DMBMMA copolymers we assumed that incorporation of DMB into the copolymer chain was exclusively *trans*-1,4- and the number of backbone carbons was composed of CH$_2$ and unsaturated >C= groups.] Naturally, for all the homopolymers, PVAc and the homologous series of PAMA (Table 3), the number of backbone carbons between functional groups under this scheme (a single methylene) is unity. Returning to Figure 1, it is evident that all the experimental K_A^{STD} values determined from the concentrated EPh solutions of the EVA, EMMA, and DMBMMA copolymers fit on a single asymptotic curve with a limiting value of ≈166 dimensionless units. Moreover, it appears that the "spacing" effect is not significant if greater than four backbone carbons are present between functional groups. Finally, steric crowding due to the increased size of the side groups in the homologous series of PAMA is reflected in the decreasing values of K_A^{STD} for a single backbone carbon (i.e., 1 on the *x*-axis).

So what are the ramifications? First, the "spacing" and "steric crowding" effects are factors that need to be considered in concentrated polymer solutions and limit accessibility of functional groups in (co)polymers, especially in the case of polymers such as PVAc, PMMA, PAMA, etc., where the functional groups are in close proximity along the chain. Most importantly, however, the limiting value of $K_A^{STD} = 166$ dimensionless units (Figure 1) determined from the concentrated EPh solutions of the copolymers is within error (estimated at $\leq 5\%$) the same as that determined previously from the low molecular weight EPh/EIB mixtures ($K_A^{STD} = 170$ dimensionless units) and the PVPh/EIB solutions ($K_A^{STD} = 168$ dimensionless units),[6] which implies that intramolecular screening is not a significant factor in this case (i.e., $0.05 \geq \gamma \geq 0.0$—experimental limitations preclude more accurate estimations in this range). In other words, the value of the intramolecular screening parameter, γ, defined as the fraction of same chain contacts that originate from the polymer chain bending back upon itself,[4,5] appears to be < 0.05. This is in marked contrast to that of the analogous miscible DMBVPh/EVA copolymer blends, where intramolecular screening was determined to be the primary factor that limits the maximum number of intramolecular hydrogen bonds formed.[4,5] In fact, the difference between the limiting value of K_A^{STD} for miscible DMBVPh/EVA copolymer blends (112 dimensionless units) and that determined from EPh/EIB mixtures ($K_A^{STD} = 170$ dimensionless units) was mainly attributed[5] to intramolecular screening and conforms to a γ value of ≈ 0.3.

The obvious question that we need to address is the following: Why does intramolecular screening appear to be an important factor in the aforementioned miscible hydrogen bonded polymer blend system but not in the case of the analogous concentrated polymer solution? Naturally, one important factor arises from the fact that only one of the components of the (co)polymer solution is "chainlike" and subject to bending back upon itself (the origin of intramolecular screening), while the other is a liquid of low molar mass, which is completely mobile and contains individual functional groups (hydrogen bond acceptors) that are not restrained by chain connectivity. However, if this was the only factor, we might anticipate a much lower value of γ than in the case of the (co)polymer blends, but not < 0.05, as implied by the experimental data reported in this communication. Differences in chain expansion of the (co)polymers in the blend compared to the solution is another factor that needs to be considered. EPh is clearly a good solvent for the (co)polymers used in this study, and it follows that significant expansion of the (co)polymer chain would lead to a reduction of the number of same-chain contacts that, in turn, would be reflected in a decrease in the value of γ over that observed in the blend. We fully recognize that chain expansion is not generally expected to be significant in solutions at the concentrations used in these studies, and this is a subject that we intend to explore soon.

Acknowledgment. The authors gratefully acknowledge the financial support of the National Science Foundation, Polymers Program and the E. I. du Pont de Nemours company.

References and Notes

(1) (a) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing: Lancaster, PA 1991. (b) Coleman, M. M.; Painter, P. C. *Prog. Polym. Sci.* **1995**, *20*, 1.

(2) Coleman, M. M.; Pehlert, G. J.; Painter, P. C. *Macromolecules* **1996**, *29*, 6820.

(3) Pehlert, G. J.; Painter, P. C.; Veytsman, B.; Coleman, M. M. *Macromolecules* **1997**, *30*, 3671.

(4) Painter, P. C.; Veytsman, B.; Kumar, S.; Shenoy, S.; Graf, J. F.; Xu, Y.; Coleman, M. M. *Macromolecules* **1997**, *30*, 932.

(5) Coleman, M. M.; Painter, P. C. *Macromol. Chem. Phys.*, in press.

(6) Coleman, M. M.; Xu, Y.; Painter, P. C. *Macromolecules* **1994**, *27*, 127.

(7) Pehlert, G. J. Ph.D. Thesis, The Pennsylvania State University, 1997.

(8) Hu, Y., unpublished results (available on request).

MA980248X