Notes

Functional Group Accessibility in Hydrogen-Bonded Polymer Blends. 3. Steric Shielding Effects

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Recent studies have shown that the accessibility of functional groups in hydrogen-bonded polymer blends is significantly affected by factors such as intramolecular screening and functional group accessibility, which are a direct consequence of chain connectivity.[1−4] Intramolecular screening results from an increase in the number of same-chain contacts due to the polymer chains bending back upon themselves. This "screening" reduces the number of intermolecular hydrogen bonds that are formed in a polymer blend versus those found in an analogous low molecular weight mixture. Moreover, other factors such as the spacing between the functional groups along a polymer chain and the presence of bulky side groups also significantly reduce the "accessibility" of the functional groups. These factors are collectively called functional group accessibility effects.

Previous studies of 2,3-dimethylbutadiene-*stat*-4-vinylphenol (DMBVPh) blends with a homologous series of poly(*n*-alkyl methacrylates) (PAMA) showed that the accessibility of the PAMA carbonyl groups decreases as the length of the PAMA side chains increases.[2] This finding is attributed to at least two factors that limit functional group accessibility: steric crowding due to the close spacing of the PAMA carbonyl groups with one another along the polymer backbone and steric shielding due to the PAMA side chains hindering access to the carbonyl groups. To separate the effects of steric crowding and steric shielding on functional group accessibility, a series of 2,3-dimethylbutadiene-*stat*-*n*-alkyl methacrylate (DMBAMA) copolymers were synthesized and blended with DMBVPh[24] (a DMBVPh copolymer containing 24 wt % VPh units).[5] The DMB segment in the DMBAMA copolymers acts an "inert" (non-hydrogen bonding) diluent, spacing the AMA segments apart to a point where the AMA segments do not interfere with one another in forming a hydrogen bond with a VPh segment of the DMBVPh[24] copolymer.[6] This "spacing" out of the AMA carbonyl groups will limit the effect of steric crowding on functional group accessibility and therefore enable us to focus on the effects of steric shielding.

In this note we present the results of blends of DMBVPh[24] with a series of DMBAMA copolymers containing AMA segments of increasing side chain length (i.e., methyl, ethyl, *n*-propyl, *n*-butyl, *n*-decyl, and *n*-hexadecyl). Miscibility of the blend systems was confirmed by visual examination (optical clarity) and thermal analysis (appearance of a single intermediate glass transition temperature). For comparison purposes, the fraction of hydrogen-bonded carbonyl groups, $f_{HB}^{C=O}$, is expressed in terms of a standard interassociation equilibrium constant, K_A^{Std}, which is based on a common reference volume of 100 cm^3/mol at 25 °C.[1−3] The experimental methodology used to accurately determine the $f_{HB}^{C=O}$ of the blend systems by curve resolving has been described in detail previously and is not repeated here.[1−3,7] The values of K_A^{Std} were determined from a least-squares fit of the $f_{HB}^{C=O}$ data to the appropriate stoichiometric equations following our standard procedure and are listed in Table 1.[1,2] The necessary parameters include the molar volume of DMBVPh[24], V_B = 525 cm^3/mol,[2] the corresponding values of the DMBVPh[24] self-association equilibrium constants at 25 °C, K_2 = 4.0 and K_B = 12.7 dimensionless units,[2] and molar volumes of the average specific repeat of the different (co)polymers, V_A, which are estimated from group contributions[1] and given in Table 1.

Table 1. Dimensionless Interassociation Equilibrium Constants

polymer	molar vol (cm^3/mol)	$K_A^{25°C}$ (h_A = −4.1 kcal/mol)	K_A^{Std} (V_B = 100 cm^3/mol, T = 25 °C)	no. of carbons[a] between funct groups
PMMA[b]	84.9	10.4	54.6	1
DMBMMA[70]	133	14.2	74.6	2.3
DMBMMA[51]	193	15.0	78.8	6.3
DMBMMA[38]	268	15.4	80.9	9.9
DMBMMA[19]	563	16.4	83.8	24.3
PEMA[b]	101	10.4	54.7	1
DMBEMA[28]	430	15.6	82.1	17.0
DMBEMA[18]	684	16.1	84.7	29.4
DMBPMA[28]	487	14.2	74.6	19.0
DMBPMA[23]	598	14.2	74.4	24.4
PBMA[b]	134	8.8	46.1	1
DMBBMA[33]	458	13.7	72.1	16.8
DMBBMA[24]	639	13.8	72.6	25.6
PDMA(b)	233	7.3	38.1	1
DMBDMA[89]	265	10.3	54.2	2.6
DMBDMA[73]	327	13.0	68.3	5.6
DMBDMA[47]	519	13.7	71.9	14.9
DMBDMA[32]	772	13.7	72.1	27.2
PHDMA[b]	332	6.3	33.1	1
DMBHDMA[88]	389	12.0	62.9	3.8
DMBHDMA[79]	425	13.1	68.7	5.5
DMBHDMA[40]	854	13.7	72.1	26.4

[a] Average number of backbone carbons between functional groups in a specific repeat unit. [b] Data from ref 2.

In Figure 1, the values of K_A^{Std} listed in Table 1 are plotted against the average number of backbone carbons between functional groups in the "specific" repeat unit (assuming that incorporation of DMB into the copolymer was exclusively *trans*-1,4- and the number of backbone carbons was composed of CH_2 and unsaturated >C= groups).[8] From this figure it is apparent that the values

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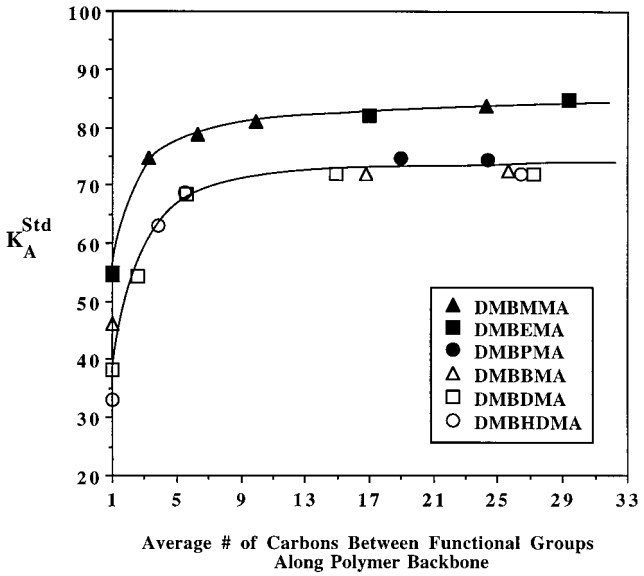

Figure 1. Plot of K_A^{Std} versus the average number of backbone carbons between functional groups for DMBVPh[24] blends with the series of DMBAMA copolymers.

of K_A^{Std} obtained from blend studies of DMBVPh[24] with DMBMMA increase asymptotically from ≈55 to 84 as a function of the average number of backbone carbons between the functional groups (the magnitude of K_A^{Std} increases from 55 for PMMA (i.e., DMBMMA[100]) to 75 for DMBMMA[70], to 79 for DMBMMA[51], to 81 for DMBMMA[38] and to 84 for DMBMMA[19]) until a plateau is reached. This is the same trend observed from previous blend studies of DMBVPh with ethylene-*stat*-vinyl acetate (EVA) and ethylene-*stat*-methyl methacrylate (EMMA) copolymers.[2,3] That is, as the spacing between the carbonyl groups along the polymer chain increases, the magnitude of K_A^{Std} increases until a plateau is reached, at which further spacing out of the carbonyl groups does not result in a further increase in the magnitude of K_A^{Std} (i.e., the "spacing" effect). The same trend is observed for the DMBEMA copolymer blends (the magnitude of K_A^{Std} increases from 55 for PEMA (i.e., DMBEMA[100]) to 82 for DMBEMA[28] and to 85 for DMBEMA[18]). This indicates that there is no difference in the accessibility of the carbonyl groups if ethyl is substituted for methyl in the side group (i.e., the values of K_A^{Std} are, within error, the same).

The results from blends of DMBVPh[24] with the DMBPMA, DMBBMA, DMBDMA, and DMBHDMA copolymers follow a similar trend as the DMBMMA and DMBEMA blends, but the value of K_A^{Std} at which the plateau is reached is significantly lower (≈74) and outside the anticipated range of error (estimated to be 5%)[2,5]—see Figure 1. This reduction in the maximum value of K_A^{Std} for the blends with DMBAMA copolymers containing longer *n*-alkyl side groups (i.e., *n*-propyl and higher) is believed to be caused by the ability of the longer side groups to "bend back" upon themselves and hinder access to the carbonyl group to some extent. In other words, a certain fraction of the allowed side chain conformations possibly shield the carbonyl group from forming a hydrogen bond with the VPh hydroxyl group.

It is also apparent from Figure 1 that the magnitude of K_A^{Std} at large spacings between the AMA segments (i.e., at the plateau) is essentially constant. This indicates that the accessibility of the AMA carbonyl groups at large spacings (number of backbone carbons >5) is dependent on the number of side chain conformations that can bend back upon themselves and not on the size of the side chain group. However, when the AMA segments are crowded closely together along the chain (number of backbone carbons ≈ 1) the magnitude of K_A^{Std} is observed to decrease as the length of the side chain increases. This latter trend is attributed to a combination of both steric crowding and steric shielding. In other words, the accessibility of the AMA carbonyl groups is reduced by the crowding together of the AMA segments and by steric shielding due to the long chain side groups bending back upon themselves. Furthermore, since the AMA units are crowded together it seems reasonable to assume that long-range steric shielding could also occur, in addition to local steric shielding and that the amount of this long-range shielding would increase as the side chain length increases. This would explain why the value of K_A^{Std} decreases as the length of the AMA side groups increases for the PAMA blends.

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(6) It should be noted that this "crowding" may not be a steric effect per se but have its origins in the loss of ability of closely spaced functional groups along the chain to orient correctly in order to form intermolecular hydrogen bonds. Spacing such groups apart with flexible "inert" units increases the rotational freedom of hydrogen-bonded functional groups with respect to their immediate same chain neighbors.
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