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The accessibility of functional groups to intermolecular hydrogen bonding in polymer blends containing a liquid crystalline polymer

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Abstract

FTIR has been utilized to examine the effect of polymer rigidity and copolymer composition on the accessibility of functional groups to form intermolecular hydrogen bonds in polymer blends. The results illustrate that the accessibility of functional groups to intermolecular hydrogen bonding increases as the distance between these groups along the polymer backbone increases, in agreement with previous studies. The results also demonstrate that an increase in the distance between hydrogen-bonding donating groups also minimizes the importance of the rigidity of the other polymer on the ability to form intermolecular hydrogen bonds. This suggests that in order to form a miscible blend between a rigid and an amorphous polymer, the functional groups that participate in hydrogen bonding should be separated along the backbone polymer chain. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid crystalline polymers; Polymer blends; Hydrogen bonding

1. Introduction

Polymer blends have attracted considerable attention recently because of their potential use as practical engineering materials with desirable properties [1]. However, mixtures of two or more polymers are often immiscible and form phase-separated, heterogeneous mixtures. This is due to the unfavorable low entropy of mixing polymers and can lead to inferior properties of the blends due to the presence of weak biphasic interfaces. It is also known that hydrogen bonding between two polymers can be utilized to improve the mixing of polymers, and thus the properties of the polymer mixture [2]. This improvement of the ultimate properties of the blend will only come about if the favorable enthalpic interaction of the hydrogen bonds is sufficient to supplement the meager entropy of mixing to overcome the unfavorable enthalpic interactions between the two polymers. Thus, a thorough understanding of the important factors that affect the amount of intermolecular hydrogen bonding that can be realized between two polymers, such as polymer rigidity and functional group accessibility, is essential for the development of new blends that utilize hydrogen bonding to induce miscibility. Pursuant to this, we have recently examined the effect of chain rigidity on the formation of intermolecular hydrogen bonds in blends of poly(styrene-*co*-vinyl phenol) (PS-*co*-VPh) and a series of polyethers with different rigidity [3].

The accessibility of functional groups to form intermolecular interactions is also an important concept in polymer blends that incorporate specific interactions [4]. Factors such as chain connectivity and steric shielding or crowding will limit the number of intermolecular interactions that can form in blends. Thus, essentially, not all functional groups of the polymers in a blend can be involved in intermolecular hydrogen bonding. This limitation, in turn, may result in a blend that can not attain sufficient intermolecular interactions to create a miscible blend. Thus, an understanding of the parameters that can be manipulated to improve functional group accessibility is required.

Coleman and Painter have provided some insight into this problem [4–6]. They have determined the accessibility of the carbonyl functional group in blends of poly(2,3-dimethylbutadiene-*stat*-4-vinyl phenol) (24% vinyl phenol) (DBPVPh) with poly(*n*-alkyl acrylate) (PAA) with different length side chains as well as with ethylene-*co*-vinyl acetate (70, 45,25, 18 wt% vinyl acetate) copolymers [5]. They utilized the inter-association equilibrium constant (K_A at 25°C) as a measure of the accessibility of the carbonyl groups for intermolecular hydrogen bonding. K_A was obtained from the FTIR spectra of the blends. A decrease in the K_A of the carbonyl group of PAA, signifying a

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decrease in the extent of intermolecular hydrogen bonding, was observed for blends of DBPVPh/PAA as the size of the side chains increased. The authors interpreted these results as evidence that the bulky side groups of the acrylates inhibit the formation of hydrogen bonds in blends by limiting the ability of the two chains to arrange and orient themselves correctly to form intermolecular hydrogen bonds. Additionally, the standard inter-association equilibrium constant for the DBPVPh/ethylene-*co*-vinyl acetate blends, and therefore the accessibility of the acetate group to form intermolecular hydrogen bonds, increases as the spacing between the vinyl acetate groups in the ethylene-*co*-vinyl acetate copolymer increases, until it reaches a maximum for a copolymer composition of 18 wt% vinyl acetate. The authors suggest that as the average distance between vinyl acetate groups increases with decreasing acetate concentration, the rotational motion of the acetate groups become independent of each other. This independence allows more acetate groups to orient themselves properly to form intermolecular hydrogen bonds. This process, of course, starts to decrease when the number of acetate groups in the copolymer become so low as to limit the possible number of intermolecular hydrogen bonds that can be created.

The effect of chain connectivity and steric crowding on the extent of hydrogen bonding in polymer solutions has also been studied by Coleman et al. [6] Solutions of poly(*n*-alkyl methacrylates) [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)] and poly(ethylene-*stat*-vinyl acetate) (70,45, 40 wt% vinyl acetate) in 4-ethyl phenol were examined. Similar to the blend systems, an increase in the accessibility of the carbonyl group to form intermolecular hydrogen bonds with the hydroxyl group of 4-ethyl phenol was observed as the spacing between acetate groups increases in the poly(ethylene-*stat*-vinyl acetate) copolymers. The results also showed the effect of steric crowding on the extent of hydrogen bonding between poly(*n*-alkyl methacrylate) and 4-ethyl phenol that is similar to the blend studies. A decrease in the K_A values was observed with an increase in the length of the alkyl group of the poly(*n*-alkyl methacrylates).

Coleman and Painter have also examined the interplay between steric crowding and spacing of functional groups along a copolymer chain on functional group accessibility. They examined blends of poly(2,3-dimethylbutadiene-*stat*-4-vinylphenol) (24, 48 and 72 wt.% vinyl phenol) and poly(*n*-alkyl methacrylates) [4]. Their results show that the spacing between the hydroxyl groups in poly(2,3-dimethylbutadiene-*stat*-4-vinylphenol) can have an important impact on the extent of intermolecular hydrogen bonding between poly(2,3-dimethylbutadiene-*stat*-4-vinyl phenol) with the other polymers, regardless of the bulkiness of the poly(*n*-alkyl methacrylates). They have also demonstrated that only a certain number of hydroxyl groups are available for hydrogen bonding. This limitation was explained as due to steric accessibility or a loss of internal degrees of rotational freedom in a chain where functional groups are hydrogen-bonded.

The objective of this study is to explore the interplay between the effect of the rigidity of one polymer and the distance between hydrogen bonding donating groups (hydroxyl groups) along the backbone chain of the other polymer on the accessibility of the hydroxyl groups to form intermolecular hydrogen bonds. This will be accomplished by utilizing infrared spectroscopy to determine the amount of intermolecular hydrogen bonding in blends of poly(styrene-*co*-vinyl phenol) (PS-*co*-VPh) and a series of polyethers. Changing the composition of the styrenic copolymer will vary the distance between hydroxyl groups as described in Section 2. The rigidity of the polymers will be altered by examining polyethers with slightly differing flexibility, including one that exhibits liquid crystalline behavior. The interpretation of these results will thus provide important insight into how changing the accessibility of the proton-donating groups in a polymer chain can alter the amount of intermolecular hydrogen bonds in blend systems that contain a liquid crystalline or rigid polymer. This, in turn, can be utilized in future studies to optimize the properties of liquid crystalline polymer mixtures.

2. Experimental

Styrene, 4-acetoxy styrene, hydrazine hydrate, phenol, chloroacetone, 1,7-dibromoheptane, tetrabutyl ammonium hydrogen sulfate (TBAHS) and 1,9-dibromononanone were purchased from Aldrich Chemical Company. Azobisisobutyronitrile (AIBN) was purchased from Dojac, Inc. 4,4′-Dihydroxy diphenylmethane was provided by Lancaster Synthesis Incorporation and used as received. 4,4′-Ethylidenebisphenol was purchased from TCI America Inc. and used as received. Poly(4-vinyl phenol) (PVPh) ($M_w = 22,000$ g/mol) was purchased from Polyscience Inc. The synthesized polymers were characterized by nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC) and gel permeation chromatography (GPC).

Proton NMR experiments were carried out on a 400 MHz Bruker NMR spectrometer using TMS as an internal standard. Differential scanning calorimetry (DSC) measurements were completed using a Mettler DSC 821 calibrated with indium at the rate of 10°C/min. The molecular weights of the polymers were determined using a Waters gel permeation chromatograph (GPC) equipped with Ultrastyragel columns with a refractive index detector. Tetrahydrofuran (THF) was used as the elution solvent and narrow dispersity polystyrene was used as calibration standards. PS-*co*-VPh (10 and 20% VPh) were synthesized by free-radical polymerization of styrene and 4-acetoxy styrene

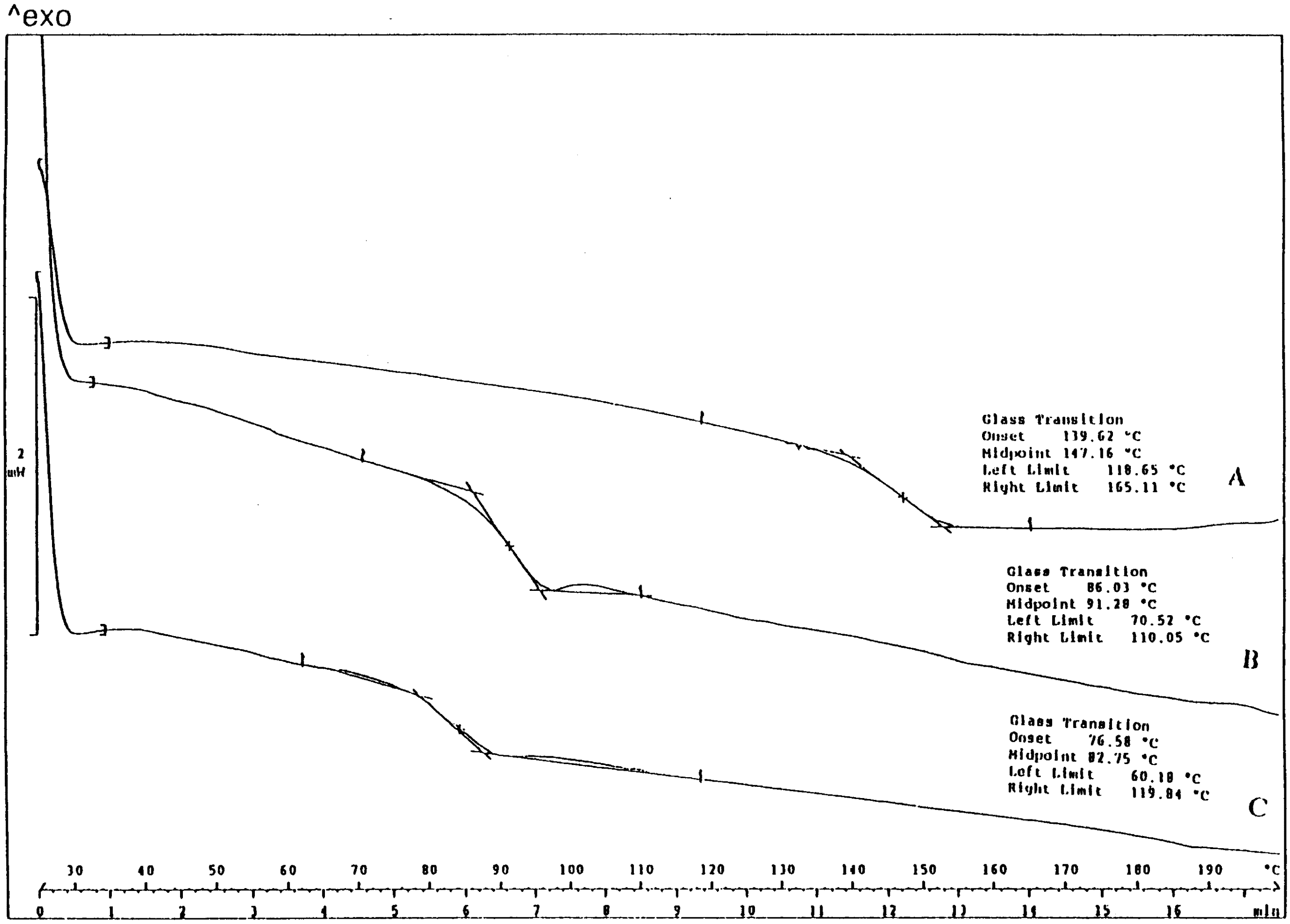

Fig. 1. DSC Thermograms of the styrenic polymers utilized in this study: (A) poly(vinyl phenol); (B) 20% PS-*co*-VPh; (C) 10% PS-*co*-VPh.

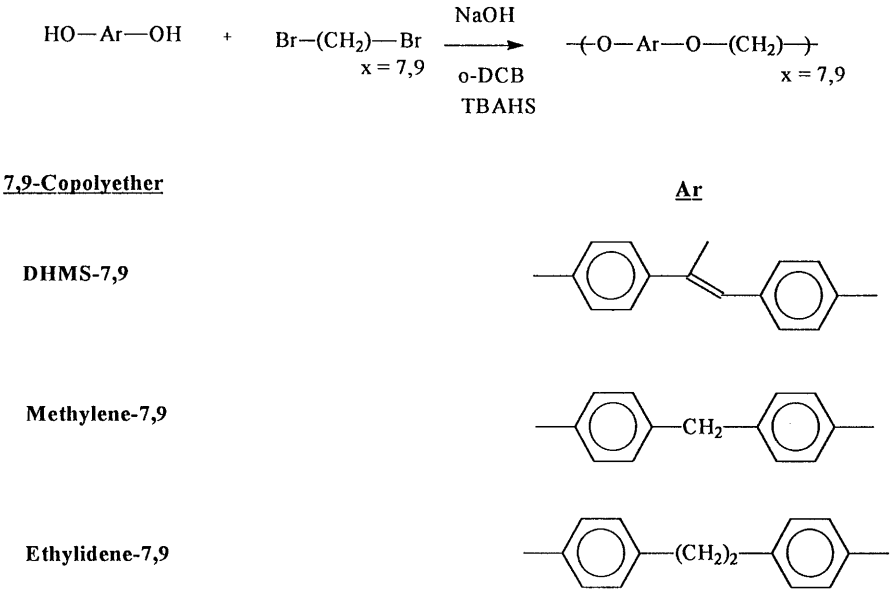

Fig. 2. Structures and synthetic scheme for the polyethers used in this study.

Table 1
Molecular weight and phase transition behavior of the three polyethers utilized in this study

Polymer	M_w	T_m (°C)	T_{n-i} (°C)
Ethylidene-7,9	24,000	60	–
Methylene-7,9	22,000	89	–
DHMS-7,9	29,000	90	190

using AIBN as the initiator. Subsequent hydrolysis of the acetoxy groups to hydroxyl groups was completed using hydrazine hydrate, as described in the literature [7]. The compositions of the copolymers were determined by ^{1}H NMR spectroscopy, which showed that the percentage of acetoxy styrene were 9.98 and 19.9% for the copolymers with 10 and 20% vinyl phenol, respectively. These copolymers will be denoted 10% PS-*co*-VPh and 20% PS-*co*-VPh. The number-average molecular weights of the 10% PS-*co*-VPh and 20% PS-*co*-VPh were found to be 24,000 and 21,900 g/mol, respectively. The reactivity ratios of styrene and acetoxy styrene are $r_1 = 0.8$ and $r_2 = 1.02$ [7], which indicates that the resultant copolymer is random in nature. In other words, the –OH groups in the final PS-*co*-VPh copolymers are evenly distributed along the polymer chain. With this knowledge, the average space between –OH monomers in the 20% PS-*co*-VPh polymer can be estimated to be five monomers, while this spacing for the 10% PS-*co*-VPh chain is 10 monomers. Thus, the average distance between hydrogen bonding sites on the amorphous copolymer is doubled as the amount of –OH in the copolymer goes from 20 to 10%.

Fig. 1 shows the DSC thermograms of 20% PS-*co*-VPh and 10% PS-*co*-VPh as curves B and C, respectively. These curves show that these polymers have glass transitions at 83 and 91°C, respectively. The PVPh used in these studies exhibited a glass transition of 147°C, also shown in Fig. 1 as curve A.

Phase-transfer polyetherification of the corresponding diphenolic compounds, 1,7-dibromoheptane, and 1,9-dibromonanoane, with tetrabutyl ammonium hydrogen sulfate (TBAHS) as a catalyst synthesized the three polyethers that were utilized in this study [8,9]. The chemical structures of the 7,9-copolyethers are shown in Fig. 2. The details of the synthesis of these three polyethers have been described in detail elsewhere [3]. The phase transition temperatures and molecular weights of the three polyethers are listed in Table 1. In particular, it is important to note that each polyether exhibits a crystalline melting point, however, only the DHMS exhibits thermotropic liquid crystallinity. Inspection of the structures and phase behavior [3] shows that the rigidity of the polymer chains decreases as one goes from DHMS-7,9 to methylene-7,9 to ethylidene-7,9 in Fig. 2. This variation in backbone rigidity will be utilized in interpreting the importance of polymer stiffness on the ability to form intermolecular hydrogen bonds in polymer blends.

The blends of PS-*co*-VPh and 7,9-copolyethers were prepared by dissolving appropriate amounts of the polymers in THF to form 2% (w/v) solutions of the 85/15 (w/w%) blends of the two polymers. Blend compositions other than 85/15 were also examined, where feasible, and similar results were found. The 85/15 samples are presented here as they were the samples that were most reliable, primarily due to the ability to analyze the –OH band in the IR spectra. At blend compositions with lower amorphous copolymer concentrations, the 10% PS-*co*-VPh and 20% PS-*co*-VPh copolymers did not exhibit strong –OH bands due to the paucity of –OH bonds present in the sample. This made the analysis described below unreliable.

Sample preparation for completion of the IR experiments consisted of solvent casting the blends on KBr disks at room temperature from THF. After a majority of the solvent had evaporated, the KBr disks were transferred to vacuum and kept there for two days to remove residual solvent. The films prepared for this study were adequately thin to be within an absorbance range where the Beer–Lambert law is satisfied. The IR spectra were recorded on an FTS-60 Bio-Rad FT-IR purged with dried air. Sixty-four scans at a resolution of 2 cm^{-1} were signal averaged and stored. The frequency scale was internally calibrated with a reference He–Ne to an accuracy of 0.2 cm^{-1} and externally with polystyrene. The curve fitting of the absorbance IR peaks were performed by PeakFit software version 3.0, upon baseline correction of absorbance IR signals. A high-temperature cell mounted in the spectrometer was employed to obtain elevated temperature spectra. The temperature was controlled to an accuracy of 0.5°C. For elevated temperature experiments, the temperature was kept constant for 30 min at a given temperature before taking the scans to ensure that the samples reached thermal equilibrium.

To qualitatively determine the extent of intermolecular hydrogen bonding, the stretching band of the hydroxyl group in the region of 3000–3700 cm^{-1} is examined. Using infrared spectroscopy, the stretching vibrations of "free" non-hydrogen bonded hydroxyl groups in pure PVPh are observed at 3525 cm^{-1}, while the stretching vibration of the hydroxyl groups that undergo hydrogen bonding to other –OH in pure PVPh can be found at 3370 cm^{-1} [10]. When the PS-*co*-VPh is in a blend with a polyether, however, other possibilities occur; the hydroxyl hydrogen can form an intermolecular hydrogen bond to ethereal oxygen. The ethereal oxygen in polyethers is more basic than the oxygen of an O–H in PVPh. This means that the intermolecular hydrogen bonding between a hydroxyl phenolic group and ethereal oxygen is stronger than that between the hydroxyl phenolic groups in pure PS-*co*-VPh. [11] Therefore, the O–H bonds involved in intermolecular hydrogen bonding with the ethereal oxygen become weaker than those involved in self-association among PS-*co*-VPh molecules. This, in turn, impacts the frequency of the stretching of the O–H band. The IR band of the stretching of a hydroxyl group that participates in intermolecular hydrogen bonding will occur at a lower frequency (a red

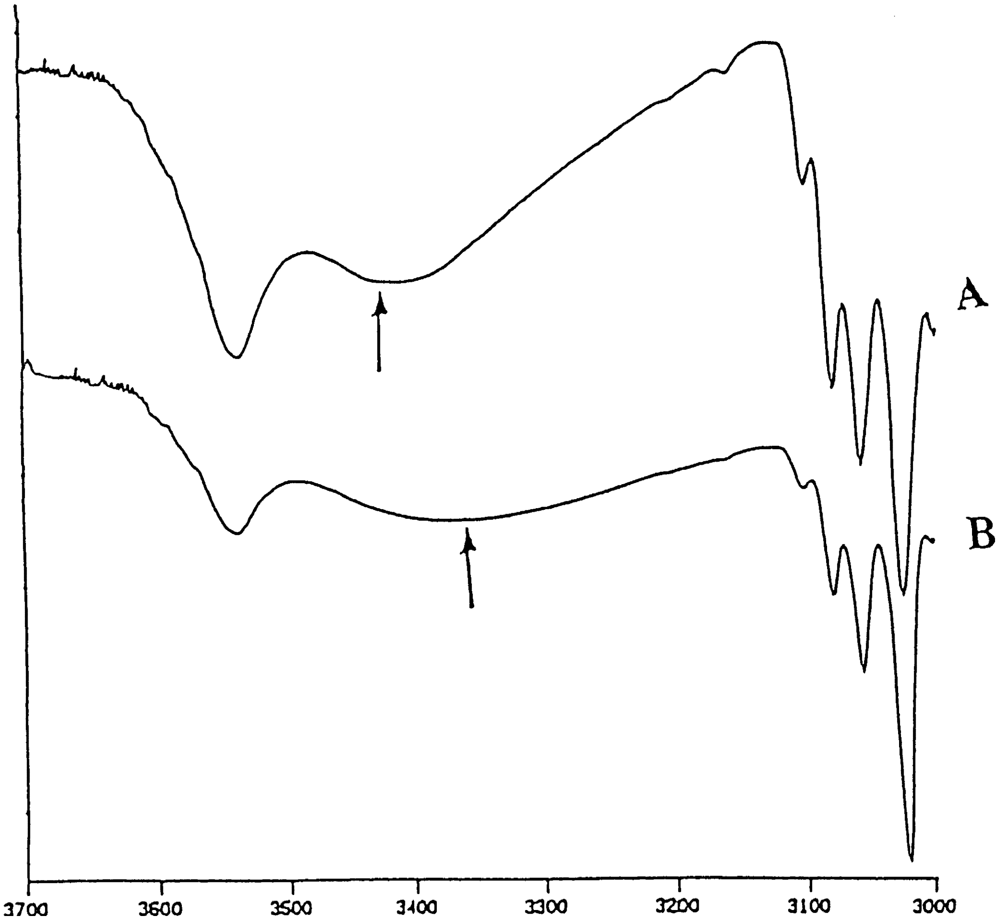

Fig. 3. FTIR spectra showing the hydroxyl stretching band for (A) an 85/15 blend of 10% PS-*co*-VPh and DHMS-7,9 and (B) neat 10% PS-*co*-VPh.

shift will occur) than that of a free or self-associated –OH group. This fact will be utilized in our analysis to determine the relative amount of intermolecular hydrogen bonding that occurs between the hydroxyl group of PS-*co*-VPh and the ether oxygen of the polyether. The frequency of the stretching of the hydrogen bonded –OH will be correlated to the amount of intermolecular hydrogen bonding with a lower frequency equating to the formation of more intermolecular hydrogen bonds.

The frequency of the IR transmittance signals at the minimum of the peaks will be used as a measure of the frequency of the shift. Thus, the frequency of the stretching of the hydrogen-bonded –OH reported in the results section were determined by fitting the experimental data of the stretching vibration of the hydrogen bonded hydroxyl group between 3150 and 3630 cm^{-1} into Gaussian functions. The curve fitting of the stretching hydroxyl signals were performed assuming both two bands (associated with free and hydrogen bonded –OH groups) and three bands (associated with free, intramolecular and intermolecular hydrogen bonded –OH groups). It is difficult to argue that the peak associated with the hydrogen-bonded –OH groups should consist of two peaks rather one, as the choice between these two options is not clear. However, it was found that there was no significant differences in the trends described below when comparing the results of the two band and three band fits. As the purpose of the curve-fitting procedure is to determine a “frequency indicator” for hydrogen-bonded hydroxyl stretching vibration, we report the results for two bands in the curve-fitting process. However, a report of the results from fits that use three –OH bands would not change the essential interpretation of the results. The absorbance spectra were linearly baseline corrected from 3150–3630 cm^{-1} where there are minimal absorbances for all blends. The baseline was fixed and not allowed to vary in the least square procedure for all spectra. The frequency of the “free” hydroxyl band was fixed at 3525 cm^{-1} as the strength of the free hydroxyl bond remains invariant in these studies.

3. The effect of spacing between hydroxyl groups on intermolecular hydrogen bonding

The availability of the proton-donating groups for intermolecular hydrogen bonding is an important factor in the extent of intermolecular hydrogen bonding that can occur in blends. For instance, in the case of PS-*co*-VPh/polyether

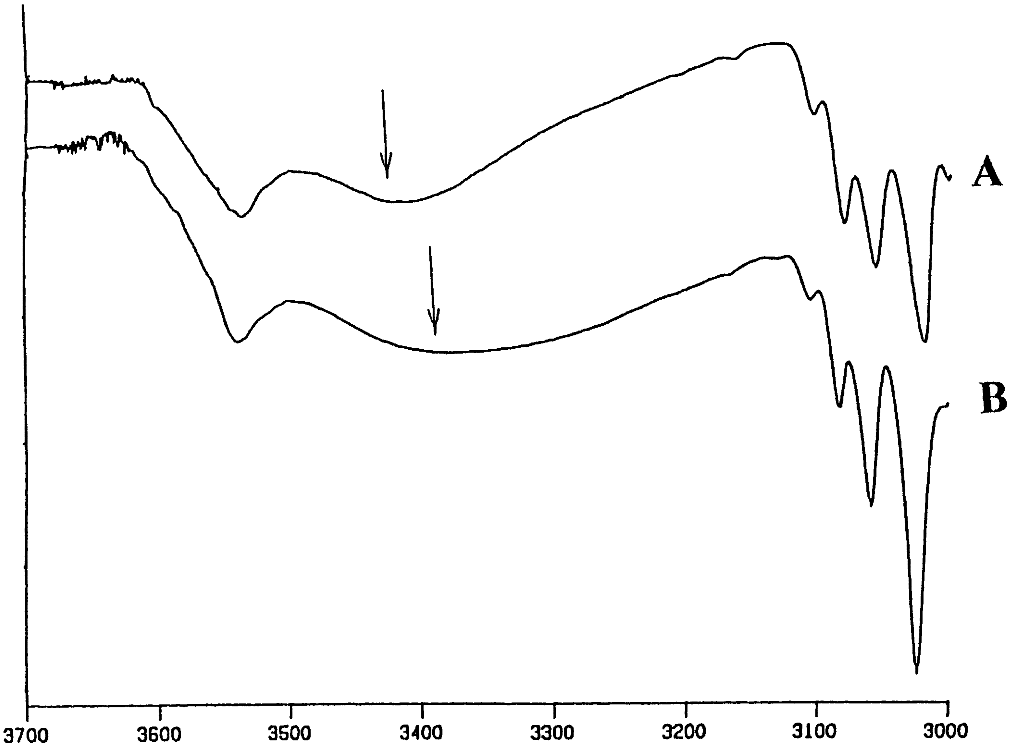

Fig. 4. FTIR spectra showing the hydroxyl stretching band for (A) an 85/15 blend of 20% PS-*co*-VPh and DHMS-7,9 and (B) neat 20% PS-*co*-VPh.

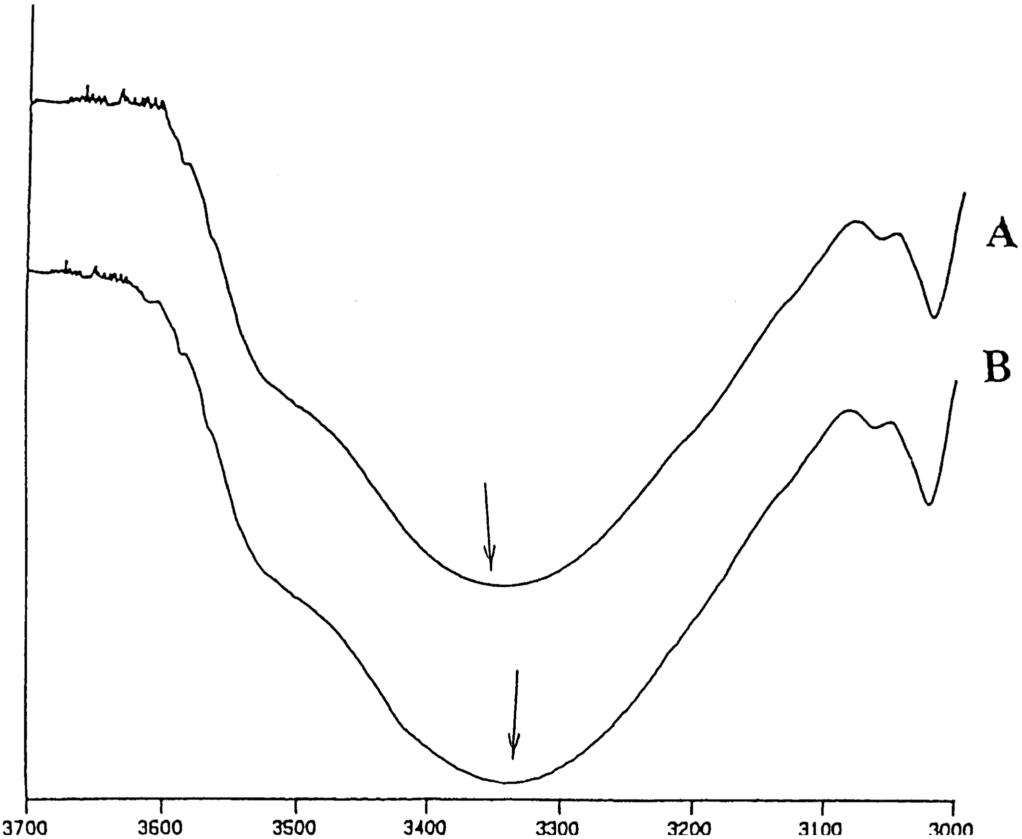

Fig. 5. FTIR spectra showing the hydroxyl stretching band for (A) an 85/15 blend of PVPh and DHMS-7,9 and (B) neat PVPh.

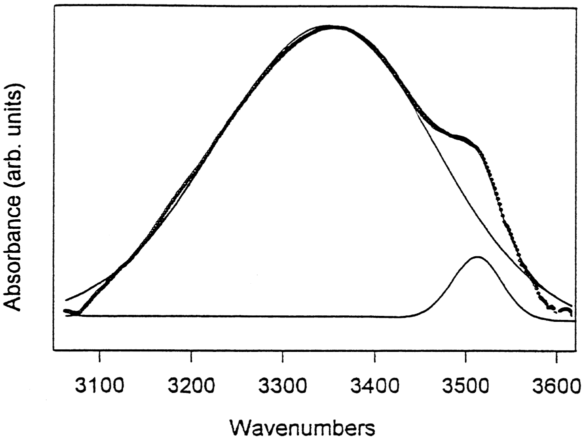

Fig. 6. An example of the curve fitting procedure for the 85/15 blend of PVPh and DHMS-7,9.

mixtures, a particular hydroxyl group on the styrenic copolymer may be adjacent to an ethereal group, but because one or more of its nearest same chain neighbors are already hydrogen-bonded to other groups, it may not be able to orient itself properly to form an intermolecular hydrogen bond.

Therefore, the effect of spacing between hydroxyl groups on the intermolecular hydrogen bonds has been examined in the blends of PS-*co*-VPh (10, 20 and 100% VPh) and three polyethers. The data for the system that includes the liquid crystalline polyether DHMS-7,9 will be presented first. The IR spectra for the stretching bands of the hydroxyl bond for the as-cast blends of 10% PS-*co*-VPh, 20% PS-*co*-VPh, and PVPh with DHMS-7,9 are shown in Figs. 3–5, respectively. The composition of each of the blends in Figs. 3–5 are 85% PS-*co*-VPh and 15% DHMS-7,9. The IR spectra of the pure styrenic polymer are also shown in these figures. The arrows in these figures denote the minima in the stretching frequency of the hydrogen-bonded hydroxyl group as determined by the curve-fitting process. An example of the result of the curve fitting procedure is shown in Fig. 6 for the blend of PVPh and DHMS-7,9.

To quantify the extent of intermolecular hydrogen bonding, the difference in the stretching frequency of the hydrogen-bonded hydroxyl band in the pure styrenic polymer and the stretching frequency of the hydrogen-bonded hydroxyl in the 85/15 blend is utilized and defined as $\Delta\nu$. Physically, the magnitude of $\Delta\nu$ is related to the proportion of the total number of hydroxyl groups that are involved in intermolecular hydrogen bonding. This physical correlation can be appreciated when it is realized that there are three contributions to the –OH band in the IR, from free hydroxyl groups (a), from hydroxyl groups that are hydrogen bonded to other hydroxyl groups (b), and from –OH groups that are hydrogen bonded to ether oxygens (c). In the pure styrenic copolymer, only (a) and (b) contribute to the IR spectra, while in the blend, (a), (b), and (c) contribute. Thus, the difference between the stretching frequency of the hydrogen-bonded hydroxyl band in the pure styrenic polymer and the stretching frequency of the hydrogen-bonded hydroxyl in the blend is a measure of the amount of intermolecular hydrogen bonding between the two components in the blend. Therefore, $\Delta\nu$ can be thought of as proportional to the probability that a given –OH group within a styrenic copolymer will have the ability to form an intermolecular hydrogen bond.

Table 2
Difference in frequency of hydrogen bonded hydroxyl bands ($\Delta\nu$) between pure PS-*co*-PVPh and PS-*co*-PVPh/7,9-copolyethers blends (85/15, w/w %)

VPh % in PS-*co*-VPh	DHMS-7,9 (cm^{-1})	Methylene-7,9 (cm^{-1})	Ethylidene-7,9 (cm^{-1})
10	79	83	91
20	44	66	73
100	39	46	64

The values of $\Delta\nu$ for the three blends of the polyethers with DHMS-7,9 as calculated from Figs. 3–5 are tabulated in Table 2. Table 2 also presents the values of $\Delta\nu$ for the blends of 10% PS-*co*-VPh, 20% PS-*co*-VPh, and PVPh with methylene-7,9 and ethylidene-7,9.

The $\Delta\nu$ values shown in Table 2 are also plotted in Fig. 7 as a function of the amount of VPh in the styrenic polymer (100% is PVPh). Inspection of the plot shows that $\Delta\nu$ increases as the VPh content in PS-*co*-VPh decreases for each of the polyethers. This can be interpreted as evidence that there is an increase in the extent of intermolecular hydrogen bonding between PS-*co*-VPh and 7,9-copolyethers as the amount of VPh decreases in the copolymer down to 10%. Remember that the average distance between the hydroxyl groups in the phenolic copolymers increases as the VPh content in PS-*co*-VPh decreases, thus these results agree, qualitatively, with those of Coleman and Painter described Section 1. It is important to note that we do not yet have data around the 10–20% composition of the styrenic copolymer and thus can not definitively state that the maximum in this plot at 10% is global. The value for $\Delta\nu$ must be 0 at 0% (i.e. polystyrene) as there is no site for an intermolecular interaction between the two polymers. Therefore, it may be that this data point at 10% is part of a peak that has a maximum between 10% VPh and 20% VPh or below 10% VPh. Indeed this peak may change with the second component of the blend (i.e. the structure of the polyether). Further experiments are in progress in our laboratory to clarify this aspect of the system.

Regardless of this, the presented results do demonstrate that as the distance between the hydroxyl groups of the PS-*co*-VPh copolymer increases, the propensity for the hydroxyl groups to form intermolecular hydrogen bonds with the polyethers improves. This may be attributed to an increase in the amount of rotational freedom of the various hydroxyl groups with respect to each other as they are further separated along the copolymer chain. A secondary factor that will also affect the accessibility of a hydroxyl group to form intermolecular hydrogen bonds is that increasing the

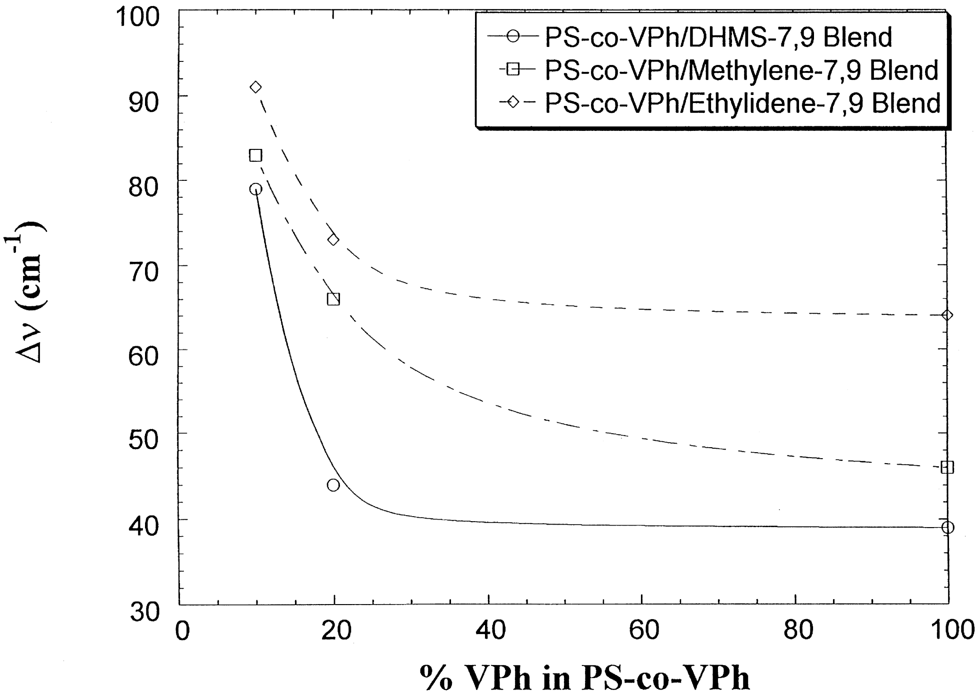

Fig. 7. Effect of spacing of the vinyl phenol groups along the copolymer chain on the intermolecular hydrogen bonding of the as-cast blends. (The lines are meant to guide the eye.)

distance between hydroxyl groups of PS-*co*-VPh also decreases the extent of intramolecular hydrogen bonding within the PS-*co*-VPh. This results in an increase in the number of the hydroxyl groups from the PS-*co*-VPh that can participate in intermolecular hydrogen bonding.

These results are for the systems as they were cast from solution. It is known, however, that blends formed by solution casting are often not equilibrium structures. To examine the effect of this possibility on the results presented above, the effect of thermal annealing above the glass transition and

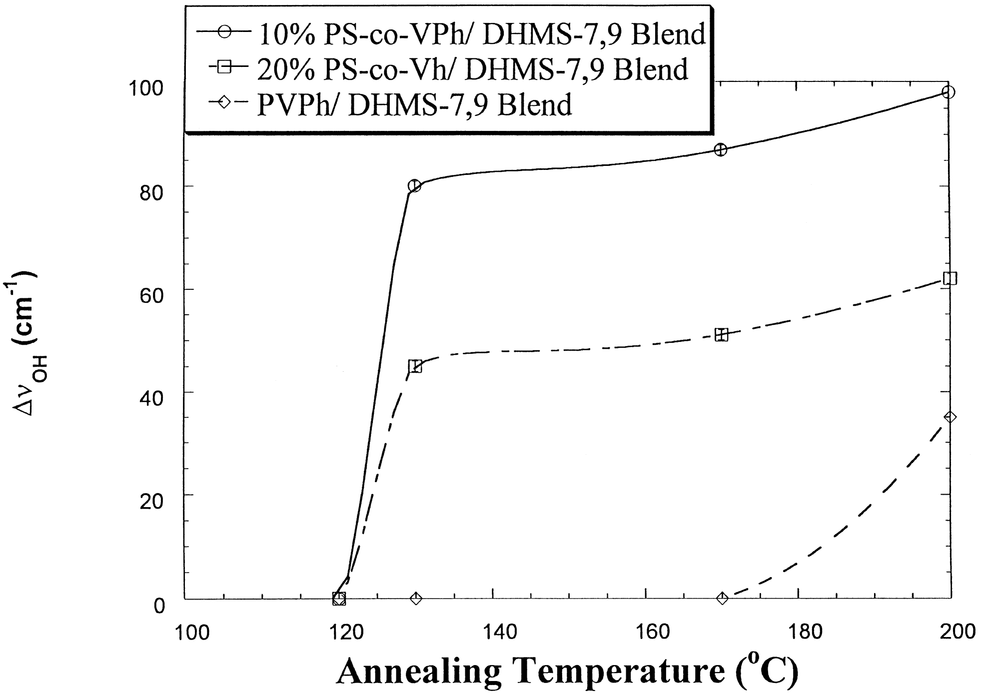

Fig. 8. Change in the wavenumber of the hydrogen bonded hydroxyl group ($\Delta\nu_{OH}$) at room temperature after high-temperature annealing.

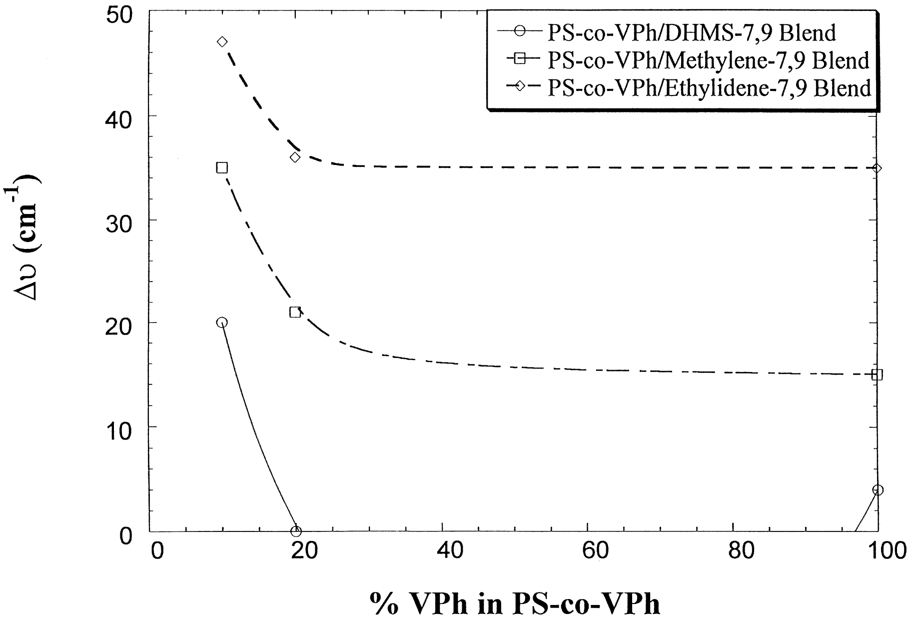

Fig. 9. Effect of spacing of the vinyl phenol groups along the copolymer chain on the intermolecular hydrogen bonding of the annealed blends.

crystalline melting temperatures of all polymers in the blend on the intermolecular hydrogen bonding and hydroxyl group accessibility has also been studied. The effect of annealing at various temperatures on the extent of intermolecular hydrogen bonding for the blends of PVPh and the three polyethers has been previously reported [3]. These results are shown in Fig. 8 as a plot of $\Delta\nu_{OH}$ vs. annealing temperature, where $\Delta\nu_{OH}$ is the difference between the minimum wavenumber of the hydrogen-bonded hydroxyl band measured at room temperature before and after annealing at the annealing temperature for 8 h. These results suggest that the crystallization of the polyethers does not dramatically influence the amount of intermolecular hydrogen bonds, as all of the copolymers melt below 90°C and the amount of intermolecular hydrogen bonding does not change up to 120°C. Additionally, it should be noted that keeping the polyether as a minor component in the 85/15 blend also minimized the crystallization of the polyether and thus its effect on the parameters studied.

The results in Fig. 8 also demonstrate that if the PVPh/DHMS-7,9 blend is annealed below 170°C for extended periods of time and then returned to room temperature, the amount of intermolecular hydrogen bonding does not change from that of the as-cast sample. However, annealing the PVPh/DHMS-7,9 blend above 170°C and returning it to room temperature does change the amount of intermolecular hydrogen-bonding from the as-cast sample. This observation was attributed to a change in the morphology of the sample with the high-temperature annealing, which may be a result of phase separation in the sample. Thus, heating the sample to a temperature below ca. 170°C does not alter the amount of hydrogen bonding from that that occurs in the as-cast sample at room temperature. However, when the blend goes above 170°C, the extent of intermolecular hydrogen-bonding is irreversibly altered. Similar annealing studies have been completed on the blends of 10% PS-*co*-VPh and 20% PS-*co*-VPh with DHMS-7,9 and are also shown in Fig. 8. Similar results were found as the PVPh blend, in that annealing these blends below a threshold temperature for extended periods of time and then returning them to room temperature did not change the amount of intermolecular hydrogen-bonding from that of the as-cast sample. However, annealing these samples above the threshold temperature irreversibly altered the amount of intermolecular hydrogen bonding. For these systems, the threshold temperature has been lowered to 130°C. It is interesting to note that the threshold temperatures (130 or 170°C) are at least 25°C above the glass or crystalline melting points of the blend components. This suggests that the as-cast samples can be annealed above the mobility temperature of all of the polymers in the blend and remain unchanged. This suggests that the initial samples are close to the equilibrium structure, however there exists a maximum temperature at which that equilibrium structure exists.

The effect of annealing above this threshold temperature on the accessibility of the hydroxyl groups to forming intermolecular hydrogen bonds has also been investigated. Pursuant to this, the blends of PVPh and the three polyethers were annealed at 200°C and the blends of 10% PS-*co*-VPh with the three polyethers and the blends of 20% PS-*co*-VPh with the three polyethers were annealed at 150°C for 8 h. After this annealing procedure, the FTIR spectra of each of the blends were obtained and analyzed to obtain $\Delta\nu$ for the blend systems after the high-temperature treatment. Fig. 9 shows the values of $\Delta\nu$ for the annealed blends as a function of the composition of the styrenic copolymer. The data in Fig. 9 shows a similar trend to that seen in Fig. 7, i.e. that an increase in the spacing of the hydroxyl groups in the PS-*co*-

VPh copolymer results in an increase in the propensity for the hydroxyl groups to form intermolecular hydrogen bonds.

4. Effect of polyether rigidity

Examination of Figs. 7 and 9 also provides some insight into the effect of the rigidity of the polyether on the extent of hydrogen bonding between the two components in the blend as well as on the accessibility of the hydroxyl groups to form intermolecular hydrogen bonds. Inspection of Fig. 7 shows that as the polyether chain becomes more rigid, the extent of intermolecular hydrogen bonds decreases. More specifically, in Fig. 7, the accessibility of the hydroxyl group (in any styrenic copolymer) to intermolecular hydrogen bonds is significantly higher in blends with ethylidene-7,9 than DHMS-7,9. Additionally, the accessibility of the –OH to intermolecular hydrogen bonds for blends containing methylene-7,9 is between that of the systems containing ethylidene-7,9 and DHMS-7,9. Thus, as the polyether in a blend becomes more flexible, if all other parameters are equal, the extent of intermolecular hydrogen bonding increases.

Taking this analysis one step further, the difference in the $\Delta\nu$ values for the DHMS-7,9 blend and the ethylidene-7,9 copolymer for a given styrenic polymer can be taken as a qualitative measure of the importance of the rigidity of the polyether (or presence of liquid crystalline behavior) on the ability of the two polymers to form intermolecular hydrogen bonds. Examination of Table 2 shows that this quantity for the blends containing PVPh is $25\ \text{cm}^{-1}$, $29\ \text{cm}^{-1}$ for the blends containing 20% PS-*co*-VPh, and $12\ \text{cm}^{-1}$ for the blends containing 10% PS-*co*-VPh. Thus, the blends that contain a polyether and 10% PS-*co*-VPh exhibit much less sensitivity of the polyether rigidity on the propensity of the two polymers to form intermolecular hydrogen bonds. This makes sense, in the fact that more separated hydroxyl groups of 10% PS-*co*-VPh have more flexibility to orient themselves correctly to form a hydrogen bond with the dynamically restricted ether oxygen of DHMS-7,9. The ether oxygen of DHMS-7,9 can be thought of as dynamically restricted due to the proximity of the stilbene group that will not allow the facile reorientation of the oxygen.

Therefore, these results suggest that one method to partially alleviate the problems of forming intermolecular hydrogen bonds between a flexible polymer and a rigid polymer may be to increase the distance along the flexible chain between the functional groups that participate in the intermolecular interactions on the flexible polymer.

5. Conclusions

FTIR has been utilized to understand the relationship between the rigidity of one polymer and the distance between functional groups along another polymer chain on the propensity for these functional groups to form intermolecular hydrogen bonds between the two polymers. The results show that an increase in the distance between functional groups yields a larger percentage of the functional groups that participate in intermolecular hydrogen bonds, in agreement with previous studies. Our interpretation of the results also reveals that when the functional groups are sufficiently separated from each other along the polymer chain, the effect of the rigidity of the other polymer becomes less important in affecting the amount of intermolecular hydrogen bonding. This suggests that to utilize hydrogen bonding to form a miscible system containing a semi-rigid (possibly liquid crystalline) polymer and an amorphous polymer, an amorphous copolymer with a low percentage of the hydrogen bonding functional group should be used to optimize the percent of functional groups that participate in intermolecular hydrogen bonding.

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