(7) Kleintjens, L. A.; Koningsveld, R. *Colloid Polym. Sci.* **1980**, *258*, 711.
(8) Guggenheim, E. A. *Mixtures*; Clarendon: Oxford, 1952.
(9) Simha, R.; Somcynsky, T. *Macromolecules* **1969**, *2*, 342.
(10) Orofino, T. A.; Flory, P. J. *J. Chem. Phys.* **1957**, *26*, 1067.
(11) Kleintjens, L. A. Ph.D. Thesis, Essex University, UK, 1979.
(12) Simha, R.; Wilson, P. S. *Macromolecules* **1973**, *6*, 908.
(13) Olabisi, O.; Simha, R. *J. Appl. Polym. Sci.* **1977**, *21*, 149.
(14) Beckman, E. J.; Porter, R. S.; Koningsveld, R., unpublished results.
(15) Simha, R.; Wilson, P. S.; Olabisi, O. *Kolloid Z. Z Polym.* **1973**, *251*, 402.

Hydrogen Bonding in Polymer Blends. 5. Blends Involving Polymers Containing Methacrylic Acid and Oxazoline Groups

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ABSTRACT: The results of a Fourier transform infrared study of poly(ethylene-*co*-methacrylic acid) (EMAA) copolymer blends with polyethyloxazoline (PEOX) are presented. EMAA copolymers are strongly self-associated at ambient temperatures through the formation of intermolecular carboxylic acid dimers. PEOX, a polymer that is inherently weakly self-associated, forms a strong association with EMAA by forming intermolecular hydrogen bonds between the carboxylic acid and oxazoline groups. These polymer blends are highly mixed at the molecular level and quantitative measurements of both the fraction of methacrylic acid and oxazoline groups that are and are not hydrogen bonded have been obtained. The results are discussed in terms of competing equilibria.

Introduction

In two previous papers of this series we have described FTIR studies of poly(ethylene-*co*-methacrylic acid) (EMAA) blends with the polyethers,[1] poly(vinyl methyl ether) (PVME), and poly(ethylene oxide-*co*-propylene oxide) (EPO), and the pyridine-containing polymers,[2] poly(2-vinylpyridine) (P2VP) and poly(styrene-*co*-vinylpyridine) (SP2VP). The presence of intermolecular carboxylic acid dimers in pure EMAA copolymers at ambient temperatures leads to strong self-association. As we have stressed previously, molecular mixing of EMAA is feasible with chemically dissimilar polymers that are inherently weakly self-associated but which contain specific sites that can potentially form favorable intermolecular interactions (notably hydrogen bonds) with EMAA. This we have described quantitatively in terms of competing equilibria.[1,2] Equilibrium constants, K_A and K_B, were employed to express the self-association of EMAA and the association of EMAA with the ether- or pyridine-containing polymer, respectively.

Miscible systems are possible even if the magnitude of K_B is much smaller than K_A. This is the case for both the EMAA–polyether and EMAA–pyridine containing polymer blends studied. K_A was determined to be approximately 2 orders of magnitude greater than K_B in the former blend system and about 40 times greater in the latter.[1,2] The relative *strengths* (ΔH) of the specific hydrogen-bonded interactions associated with the carboxylic acid dimer (AA) and the carboxylic acid–ether pair (AB), however, are of similar magnitudes and that of the analogous carboxylic acid–pyridine interaction is significantly stronger than the carboxylic acid dimer. Again, without wishing to belabor the obvious, a knowledge of the relative strengths of the specific interactions alone is not sufficient and we must recognize that there is an entropic contribution (ΔS) to hydrogen bond dissociation and formation which is an integral part of the definition of the equilibrium constant.

In this paper we present FTIR studies of EMAA–polyethyloxazoline (PEOX) blends. The unique feature of this study concerns the amount of information that can be extracted from the infrared spectra as compared to the analogous studies of the EMAA–polyether[1] or EMAA–polypyridine[2] blends. In the former system it was only possible to quantitatively measure the fraction of EMAA carbonyl groups involved in hydrogen-bonded interactions with ether groups. Normal modes containing significant contributions to their potential energy distribution from displacements involving ether oxygen atoms tend to be highly mixed and are thus conformationally sensitive. Accordingly, changes in frequency, breadth, and intensity of these modes that we might observe in the spectra of our polymer blend systems do not lend themselves to straightforward analysis and are not amenable for the quantitative analysis of specific interactions. On the other hand, in the EMAA–polypyridine system it was only possible to directly measure the fraction of pyridine groups that were or were not hydrogen-bonded. In this case specific localized modes of the pyridine ring are sensitive to hydrogen bonding. Conversely, there were unexpected complications in the carbonyl stretching region of the infrared spectra especially in polypyridine-rich blends. Separate contributions attributed to carboxylic acid dimers and carboxylic acid–pyridine interactions were not found over the whole composition range, and it was not possible to use this region of the spectrum for quantitative analysis. The particular chemical structure of the EMAA–PEOX system, however, permits us to measure both the fraction of EMAA and PEOX groups that are and are not hydro-

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gen-bonded. This permits a more rigorous test of our equilibrium models.

Experimental Section

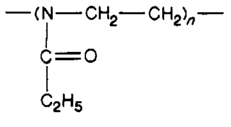
The ethylenemethacrylic acid copolymer used in this study contains 44 wt % methacrylic acid (denoted EMAA[44]) and was synthesized in the laboratories of the E.I. du Pont de Nemours Co. This polymer, which has been described previously,[1] is amorphous with a glass transition temperature (T_g) of 28 °C. Poly(ethyloxazoline) (PEOX) with a weight-average molecular weight of 200 000 was obtained from the DOW Chemical Co. It too is an amorphous polymer with a T_g of 70 °C. Both polymers are soluble in tetrahydrofuran (THF) at room temperature.

Infrared spectra were recorded on a Digilab Model FTS-60 Fourier transform infrared (FTIR) spectrometer at a resolution of 2 cm^{-1}. A minimum of 64 scans were signal averaged, and the spectra were stored on a magnetic disc system. Spectra recorded at elevated temperatures were obtained by using a SPECAC high-temperature cell mounted in the spectrometer and a Micristar heat controller. Samples for FTIR analysis were prepared by solution casting onto KBr windows from a 1% (w/v) in dry THF. To ensure an even film thickness, a saturated THF vapor environment was maintained during the evaporation process. Both polymers are hydrophillic, and care was exercised to minimize the absorption of water. Accordingly, the samples were heated under reduced pressure in a vacuum oven at 80 °C for 3 h immediately prior to recording the infrared spectrum. Thermal analysis was performed on a Perkin-Elmer 7 Series differential scanning calorimeter. A heating rate of 20 °C/min. was employed by using a sample size of approximately 10–15 mg.

Results and Discussion

A summary of the major temperature-dependent infrared spectral features attributed to the methacrylic acid structural unit has been presented in the previous paper of this series.[1] Figure 1 shows the infrared spectrum of pure EMAA[44]. The well-established and characteristic bands indicative of EMAA self-association ascribed to intermolecular carboxylic acid dimers are evident at about 3100 (ν_s(O—H)), 2650 ("satellite" bands), and 1700 cm^{-1} (ν_s(C═O)). Infrared bands attributed to unassociated carboxylic acid groups ("monomers") occur at 3530 (ν_s(O—H)) and 1750 cm^{-1} (ν_s(C═O)), respectively. At room temperature the concentration of "monomers" is very low and the bands are barely detectable.[1] It should be emphasized that we are restricted to a limited temperature range because cyclic and linear anhydrides are formed at temperatures exceeding about 140 °C. In addition, we should mention that there is a minor concentration of ester groups in the EMAA[44] copolymer which is detectable by a small shoulder at 1735 cm^{-1}. This contribution to the carbonyl stretching region of the spectrum was subtracted in a manner described previously.[1]

PEOX may be described as a tertiary amide polymer.[3] The chemical structure of the polymer is quite simple and is depicted below:



$$\text{—(N—CH}_2\text{—CH}_2)_n\text{—, N—C(═O)—C}_2\text{H}_5$$

We were unable to find any detailed infrared analysis of PEOX. However, a vibrational analysis of an analogous low molecular weight model compound, namely, *N*,*N*-dimethylpropionamide (DMP), has been performed.[4] For our purposes only the modes in the carbonyl stretching region of the spectrum are relevant. In the spectrum of PEOX (Figure 1) the dominant band at 1645 cm^{-1} corresponds to a mode occurring at 1668 cm^{-1} in the model DMP. This latter band is a mixed mode with an approximate potential energy distribution of 60% C═O stretch and 20% C—N stretch.[4] For simplicity, we will refer to this mode in the spectrum of PEOX as the PEOX carbonyl band.

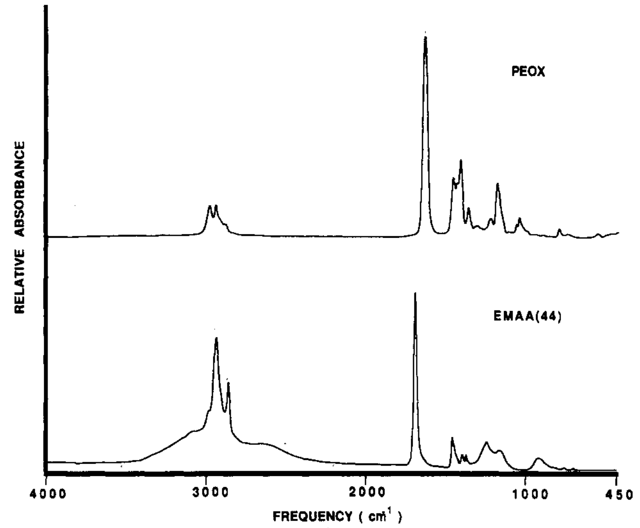


Figure 1. Infrared spectra recorded at room temperature in the range 450–4000 cm^{-1} of film samples: (bottom) EMAA[44] and (top) PEOX.

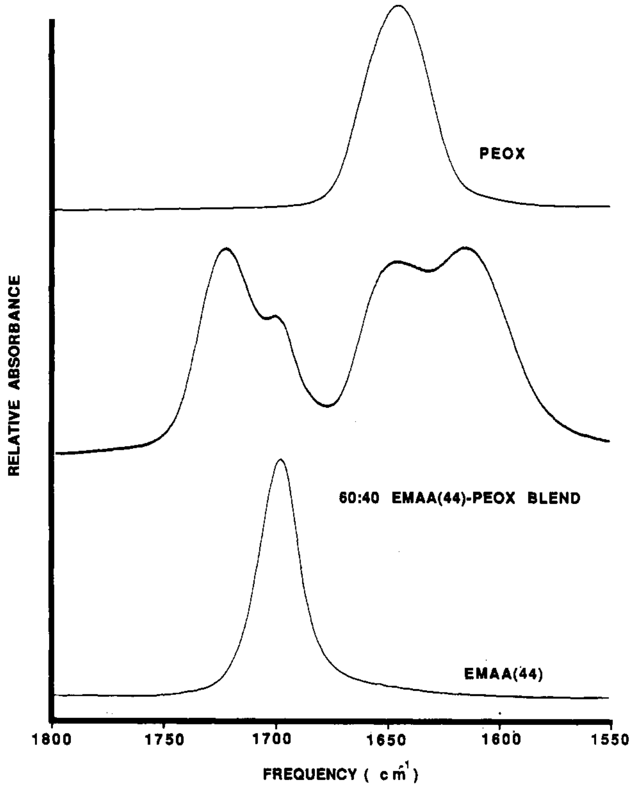


Figure 2. Scale-expanded infrared spectra recorded at room temperature in the carbonyl stretching region between 1550 and 1800 cm^{-1} of film samples: (bottom) EMAA[44]; (middle) 60:40 EMAA[44]-PEOX blend by weight, and (top) PEOX.

In any event, the most salient point is that the different carbonyl bands associated with the EMAA carboxylic acid dimer and the PEOX oxazoline groups are well-resolved

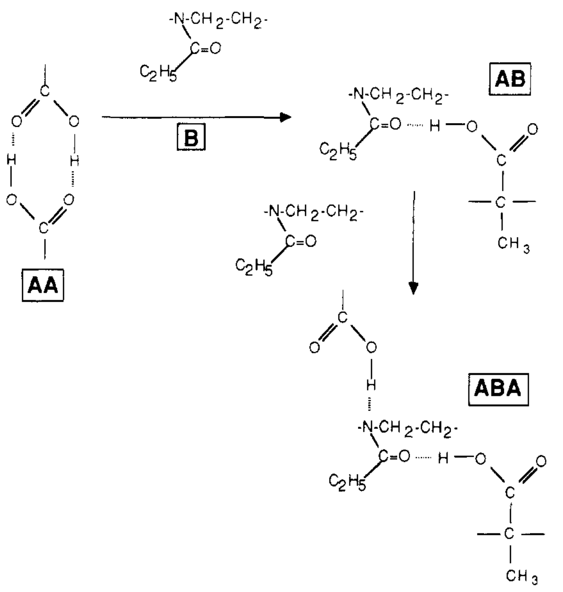


Figure 3. Schematic diagram illustrating the carboxylic acid–oxazoline interaction.

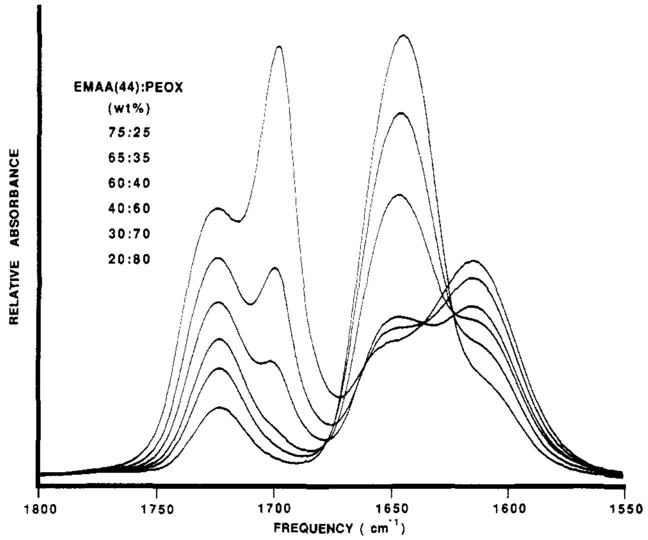


Figure 4. Scale-expanded infrared spectra in the 1550–1800 cm^{-1} region obtained on films of EMAA[44]–PEOX blends recorded as a function of composition: (A) 75:25; (B) 65:35; (C) 60:40; (D) 40:60; (E) 30:70, and (F) 20:80 wt %.

and separated by some 50 cm^{-1} as illustrated in Figure 2. Also shown in Figure 2 is the infrared spectrum of a sample of a 60:40 EMAA[44]–PEOX blend by weight. In addition to the two bands attributed to the carboxylic acid dimer (AA) and the unassociated oxazoline (B) groups (1698 and 1645 cm^{-1}, respectively), two new bands are evident at 1724 and 1614 cm^{-1}. Both of these bands may be considered as measures of the intermolecular interactions occurring between the carboxylic acid and oxazoline groups. They have a different character, however. In the former case the 1724 cm^{-1} band is a liberated or "free" EMAA carbonyl group (AB) formed when the hydroxy group of the acid associates with the PEOX carbonyl group. This is shown schematically in Figure 3. On the other hand, the 1614 cm^{-1} band is assigned to PEOX carbonyl groups that are hydrogen-bonded to the EMAA hydroxyls of the carboxylic acid groups (BA, which is equivalent to AB). There are, however, two possible PEOX sites for hydrogen bonding to the EMAA carboxylic acid group, the carbonyl oxygen and the nitrogen atoms. Evidence from model compound studies favors the former.[5,6] Nonetheless, as we will see later, in EMAA-rich blends our results suggest the presence of a significant fraction of 2:1 EMAA–PEOX complexes (denoted ABA).

Figure 4 shows arbitrarily scaled infrared spectra of a series of EMAA[44]–PEOX blend samples of different compositions recorded at room temperature. With increasing concentration of PEOX, the relative contribution to the band envelope from the mode at about 1725 cm^{-1} (the band attributed to the "complexes" AB and/or ABA) increases relative to that of the 1698 cm^{-1} mode (AA). Similarly, with increasing EMAA concentration, the contribution to the envelope from the mode at about 1614 cm^{-1} (BA) increases relative to that of the mode at 1645 cm^{-1} (B).

We are now in a position to attempt the quantitative measurement of the number of specific interactions present in a methacrylic acid–oxazoline polymer blend system as a function of composition. The spectra obtained were of excellent quality, and it was a straightforward task to draw a linear base line from 3800 to 500 cm^{-1} through regions where there is little or no absorption. The four bands in the 1550–1800 cm^{-1} region are relatively broad and essentially Gaussian in character. To minimize error as a function of composition, the curve fitting was performed separately in two regions of the spectrum—the first involving the EMAA carbonyl groups (between 1740 and 1680 cm^{-1}) and the second involving the PEOX carbonyl groups (between 1640 and 1590 cm^{-1}).

Table I summarizes the results of a least-squares curve fitting of the carboxylic acid carbonyl stretching region of the spectra. Since at room temperature there is no detectable contribution from "monomeric" carboxylic acid groups (1750 cm^{-1}), the fraction of "free" EMAA carbonyl groups, f_F^{CO} (which directly measures the fraction of carboxylic acid groups involved in intermolecular hydrogen bonding with the oxazoline groups), is given by

$$f_F^{CO} = \frac{A_{AB}}{\left[A_{AB} + \dfrac{a_{AB}}{a_{AA}}A_{AA}\right]}$$

where A_{AB} and A_{AA} are the areas of the 1724 and 1698 cm^{-1} bands, respectively (see Table I), and a_{AA} and a_{AB} are the absorptivities of the two bands. We have assumed an absorptivity ratio, a_{AB}/a_{AA}, of 1.6—a value experimentally determined for the analogous EMAA–polyether blends.[1] Estimates of the fraction of "free" EMAA[44] C=O groups range from 0.56 to 0.90 as the mole fraction of PEOX is increased from 0.33 to 0.89 in the blends.

Table II summarizes similar results of a least-squares curve fitting of the oxazoline carbonyl stretching region of the spectra. The fraction of "free" oxazoline groups, f_F^{OX} (i.e., those PEOX oxazoline carbonyl groups not hydrogen bonded to EMAA[44] carboxylic acid groups), is defined as

$$f_F^{OX} = \frac{A_B}{\left[A_B + \dfrac{a_B}{a_{BA}}A_{BA}\right]}$$

where A_B and A_{BA} are the areas of the 1650 and 1615 cm^{-1} bands, respectively (see Table II), and a_{BA} and a_B are the absorptivities of the two bands. There is reason to be confident that little error will be introduced if the same absorptivity ratio is assumed; i.e., $a_{BA}/a_B = 1.6$, the rationale being that we are concerned with carbonyl groups that are or are not hydrogen bonded to the same type of hydroxy group attached to EMAA carboxylic acid moieties.

Table I
Curve-Fitting Results of the EMAA[44]-PEOX Blends

wt % EMAA[44]: PEOX	mol fractn EMAA	"free" C=O band			carboxylic acid dimer C=O band			fractn AB[b]
		freq[a]	width[a]	area	freq[a]	width[a]	area	
80:20	0.67	1725	27	776	1698	20	985	0.56
75:25	0.6	1725	27	677	1698	20	732	0.60
65:35	0.48	1724	27	696	1698	20	449	0.71
60:40	0.43	1723	27	846	1698	20	369	0.79
50:50	0.34	1723	27	637	1698	20	191	0.84
40:60	0.25	1723	27	711	1698	20	164	0.87
30:70	0.18	1723	27	401	1698	20	78	0.89
20:80	0.11	1722	27	219	1698	20	41	0.90

[a] Wavenumber. [b] Absorbance ratio = 1.6.

Table II
Curve-Fitting Results of the EMAA[44]-PEOX Blends

wt % EMAA[44]: PEOX	mol fractn EMAA	uncomplexed PEOX C=O band			complexed PEOX C=O band			fractn B[b]
		freq[a]	width[a]	area	freq[a]	width[a]	area	
80:20	0.67	1656	35	384	1614	44	968	0.39
75:25	0.6	1655	35	368	1614	44	875	0.40
65:35	0.48	1654	35	508	1614	44	1020	0.44
60:40	0.43	1652	35	858	1613	44	1321	0.51
50:50	0.34	1650	35	1006	1612	44	1047	0.61
40:60	0.25	1649	35	1759	1611	44	1210	0.70
30:70	0.18	1648	35	1694	1609	44	698	0.80
20:80	0.11	1647	35	1834	1606	44	415	0.88

[a] Wavenumber. [b] Absorbance ratio = 1.6.

We recognize that this is a potential source of error that might affect absolute numbers but not the overall trend. The estimated fraction of "free" oxazoline groups in the blends of varying molar composition are included in Table II. The fraction of oxazoline groups involved in intermolecular interactions with the EMAA carboxylic acid groups range from approximately 0.39 to 0.88 as the molar composition of POEX in the blend increases from 0.33 to 0.89.

Theoretical Considerations—Competing Equilibria

In common with our previous studies of the analogous EMAA blends containing polyethers[1] and polypyridines,[2] we will initially consider a very simple scheme based upon two competing equilibria. Implicit is the assumption that only 1:1 complexes are formed.

$$A + A \overset{K_A}{\rightleftharpoons} AA$$

$$A + B \overset{K_B}{\rightleftharpoons} AB \qquad (1)$$

The equilibrium constants may be expressed as

$$K_A = \frac{\xi_{AA}}{\xi_A^2} \qquad K_B = \frac{\xi_{AB}}{\xi_A \xi_B} \qquad (2)$$

where ξ_A, ξ_B, ξ_{AA}, and ξ_{AB} are the mole fractions of A, B, AA, and AB units, respectively, in the mixture at equilibrium. Where "chains" of hydrogen-bonded groups are formed,[7,8] equilibrium constants are more correctly defined in terms of molar concentrations.[9] As Sarolea-Mathot[10] has shown, however, the errors involved using mole fractions are not large in simple monomer–dimer systems. We will use the simple mole fraction approach here and present a more rigorous description of the thermodynamics of these systems in a separate publication.

X_A, the initial mole fraction of A units in the blend, may be expressed as

$$X_A = \frac{(1 + K_B)\xi_A + 2K_A\xi_A^2 + K_A K_B \xi_A^3}{1 + 2K_B\xi_A + (K_A - K_B)\xi_A^2} \qquad (3)$$

We have independently determined[1] the magnitude of the equilibrium constant at room temperature for the pure EMAA copolymer ($K_A = 2 \times 10^4$). Thus eq 3 may then be solved numerically for a given value of K_B. Using appropriate values of ξ_A, one may now calculate X_A over the range from zero to unity. Corresponding calculations of ξ_{AA}, ξ_B, and ξ_{AB} are now readily performed.

We need to relate these theoretical calculations directly to the information obtained from our infrared measurements. Fortunately, this is quite straightforward. In common with our previous definitions[1,2] the *theoretical* fraction of "free" EMAA carbonyl groups, f_F^{CO}, is defined as $\xi_{AB}/(\xi_A + \xi_{AB} + 2\xi_{AA})$. Similarly, the theoretical fraction of "free" oxazoline groups, f_F^{OX}, is defined as $\xi_B/(\xi_B + \xi_{AB})$.

A comparison of the experimental blend data (Tables I and II) with theoretical curves of the fraction of "free" oxazoline and methacrylic acid groups versus molar composition of EMAA[44] in the blend are displayed graphically in Figure 5. Multiple samples were analyzed (at least three at each composition), and the error bars shown in Figure 5 reflect our best estimate of the errors arising from the curve-fitting procedure in the quantitative infrared measurements over the whole composition range. The experimental data obtained in the oxazoline carbonyl region of the infrared spectrum (Table II) follows beautifully the theoretical curves calculated for a K_B value of approximately 400. Unfortunately this is matched by a terrible fit of the data obtained from the EMAA carbonyl region (Table I). The data do not even come close to matching the curve generated for a K_B value of 400 or any other value for that matter. We can do no better than this using the simple two competing equilibria denoted in (1) above. The most important point is that the experimentally determined fraction of "free" EMAA carbonyl groups

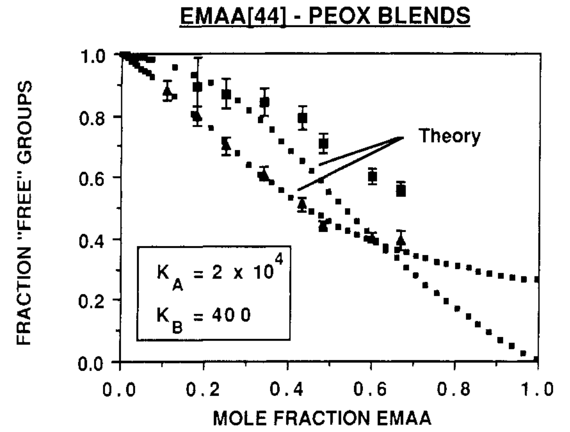


Figure 5. Plot of the fraction of "free" oxazoline groups [▲] and "free" methacrylic acid groups [■] versus the mole fraction of EMAA[44] in blends with PEOX at room temperature. The small squares are calculated by using a value of K_B = 400.

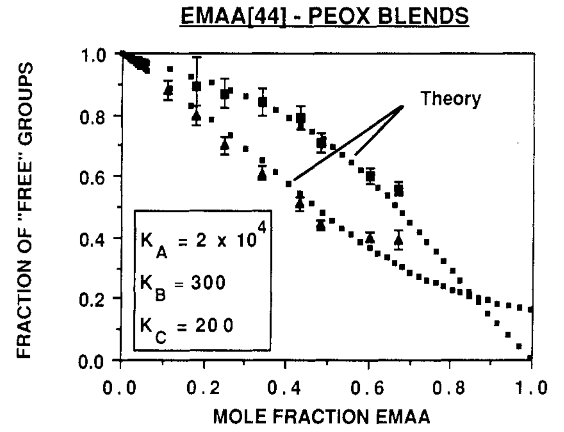


Figure 6. Plot of the fraction of "free" oxazoline and methacrylic acid groups versus the mole fraction of EMAA[44] in blends with PEOX at room temperature. The small squares are calculated by using values of K_B = 300 and K_C = 200.

is much greater in EMAA-rich blends than that calculated—a result that strongly suggests that the concentration of 2:1 "complexes" (ABA) might be significant.

We now consider the following equilibrium scheme:

$$A + A \overset{K_A}{\rightleftharpoons} AA$$

$$A + B \overset{K_B}{\rightleftharpoons} AB$$

$$A + AB \overset{K_C}{\rightleftharpoons} ABA$$

In addition to the two equilibrium constants defined in (2) above, a third K_C is now defined as

$$K_C = \frac{\xi_{ABA}}{\xi_{AB}\xi_A} \qquad (5)$$

where ξ_A, ξ_{AB}, and ξ_{ABA} are the mole fractions of A, AB, and ABA units, respectively, in the mixture at equilibrium. Now

$$\xi_A + \xi_B + \xi_{AA} + \xi_{AB} + \xi_{ABA} = 1 \qquad (6)$$

and

$$X_A = \frac{\xi_A + 2\xi_{AA} + \xi_{AB} + 2\xi_{ABA}}{\xi_A + \xi_B + 2\xi_{AA} + 2\xi_{AB} + 3\xi_{ABA}} \qquad (7)$$

By recasting this equation using the relationships given above in 2, 5, and 6, we arrive at an analogous equation to that of 3 in which X_A is expressed in terms of ξ_A and the three equilibrium constants K_A, K_B, and K_C. Knowing the magnitude of the equilibrium constant at room temperature for the pure EMAA copolymer ($K_A = 2 \times 10^4$), we can now solve numerically for given values of K_B and K_C. Again using appropriate values of ξ_A, one may now calculate X_A over the range from zero to unity and subsequently ξ_{AA}, ξ_B, ξ_{AB}, and ξ_{ABA}.

The *theoretical* fraction of "free" EMAA carbonyl groups is now defined as

$$f_F^{CO} = \frac{\xi_{AB} + 2\xi_{ABA}}{\xi_A + \xi_{AB} + 2\xi_{AA} + 2\xi_{ABA}}$$

Similarly, the theoretical fraction of "free" oxazoline groups is defined as

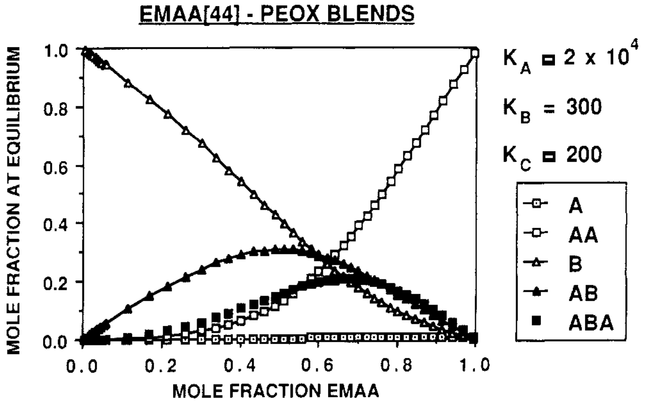


Figure 7. Calculated distributions of the mole fraction of A, AA, B, AB, and ABA species versus the mole fraction of EMAA[44] in blends with PEOX at room temperature assuming K_A, K_B, and K_C values of 2 × 10^4, 300, and 200, respectively.

$$f_F^{OX} = \frac{\xi_B}{\xi_B + \xi_{AB} + \xi_{ABA}}$$

Using as a starting point the values of K_B = 400 and K_C = 0, which corresponds to the curves displayed in Figure 5, values of K_B and K_C were systematically varied to yield a best fit of both sets of experimental data (Tables I and II). A comparison of the experimental data and the theoretical curves generated assuming values of K_B = 300 and K_C = 200 is shown in Figure 6. We fully recognize that by introducing another variable, K_C, we inevitably increase our chance of obtaining a superior fit. Nonetheless, the fit is remarkably good and we have confidence in this result since common sense dictates that oxazoline groups have two obvious sites for hydrogen-bonding interactions with labile protons.

Having reasonable estimates of the three equilibrium constants K_A (2 × 10^4), K_B (300), and K_C (200), we can now calculate the mole fraction of the species A (acid monomer), AA (acid dimer), B (uncomplexed oxazoline), AB and ABA (acid–oxazoline complexes) as a function of blend composition. This is illustrated in Figure 7. The low concentration of acid monomers (A) throughout the entire composition range is consistent with a large value of K_A. With increasing concentration of EMAA[44] in the blend, the mole fraction of acid dimers increases while that of the uncomplexed oxazoline groups decreases. Concomitantly, the fraction of acid–oxazoline AB species rises to a maximum at a blend composition of 50 mol % EMAA[44] and then decreases in the manner of a bell-shaped curve. The fraction of ABA species has the form of a skewed curve with a maximum value at about 66 mol % EMAA[44]—i.e., in EMAA-rich blends.

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Registry No. EMAA, 25053-53-6; PEOX, 25805-17-8.

References and Notes

(1) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 346.
(2) Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 954.
(3) Chiu, T. T.; Thill, B. P.; Fairchok, W. J. Advances in Chemistry 213; American Chemical Society: Washington, DC, 1986; pp 425–432.
(4) Venkata Chalapathi, V.; Venkata Ramiah, K. *Curr. Sci.* **1968**, *16*, 453.
(5) Schmulbach, C. D.; Drago, R. S. *J. Phys. Chem.* **1960**, *64*, 1956.
(6) Bull, W. E.; Madan, S. K.; Willis, J. E. *Inorg. Chem.* **1963**, *2*, 303.
(7) Coleman, M. M.; Skrovanek, D. J.; Hu, J.; Painter, P. C. *Macromolecules* **1988**, *21*, 59.
(8) Painter, P. C.; Park, Y. H.; Coleman, M. M. *Macromolecules* **1988**, *21*, 66.
(9) Flory, P. J. *J. Chem. Phys.* **1944**, *12*, 425.
(10) Sarolea-Mathot, L. *Trans. Faraday Soc.* **1953**, *49*, 8.

Notes

New Route to the Synthesis of 2-(2-Hydroxy-3-vinyl-5-methylphenyl)-2*H*-benzotriazole

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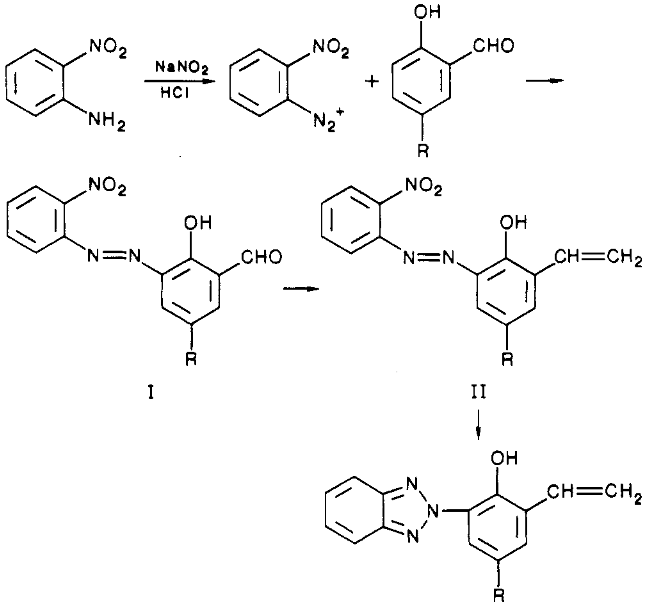
Introduction

Many polymers tend to degrade on prolonged exposure to ultraviolet light, and many classes of compounds, collectively referred to as "UV stabilizers", have been examined as additives to such polymers in attempts to improve the resistance of the polymers to degradation by ultraviolet light.

It is known[1] that compounds that comprise the 2-(2-hydroxyphenyl)benzotriazole group are particularly useful as UV stabilizers. However, there is a tendency for such 2-(2-hydroxyphenyl)benzotriazoles to be poorly compatible with polymer chains, with the result that they separate from the polymer and their effectiveness is reduced. It has been proposed[2] that the poor compatibility may be overcome by incorporating a vinyl substituent in the 2-(2-hydroxyphenyl)benzotriazole such that at least in the case of addition polymers, the UV stabilizers might be copolymerized into the polymer backbone. Methods have been reported in the literature[3,4] for the synthesis of 2-(2-hydroxyphenyl)benzotriazoles bearing such groups as methacryloylamino, acryloylamino, allyloxy, vinylsulfonyl, and vinyloxy groups, which allow such benzotriazoles to be copolymerized with conventional vinyl monomers. For example, the preparation of 2-(5-vinyl-2-hydroxyphenyl)benzotriazole by a six-step sequence and the copolymerization thereof with styrene and methyl methacrylate, as well as the synthesis of 2-(hydroxyphenyl)benzotriazole compounds having polymerizable unsaturated groups on the phenyl ring of the benzotriazole group, have been reported.[5]

We have now devised a simple three-step process for the preparation of 2-(vinylhydroxyphenyl)benzotriazoles.

Scheme I



Results and Discussion

The process for the preparation of 2-(vinylhydroxyphenyl)benzotriazoles is reported in Scheme I.

The suitable diazotized nitroaniline that is used in the first step of the process is 2-nitroaniline, and the diazo-