Complexation of Poly(*N*,*N*-dimethylacrylamide) and Phenol–Formaldehyde Resins

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ABSTRACT: Complexation between phenol–formaldehyde (PHMP) resins and poly(*N*,*N*-dimethylacrylamide) (PDMA) via hydrogen bond formation was studied. The mutual precipitates obtained from acetone, dioxane, and ethyl acetate solutions have compositions very close to simple molar ratios of the components. The glass transition temperatures of the complexes are higher than the T_g values of either component. PDMA also forms complexes with *p*-methoxy-PHMP. Again the compositions of the precipitates can be represented by simple molar ratios and the T_g's of the complexes are higher than the component T_g values. Even when the density of the hydroxyl groups in PHMP is reduced by 40%, through methylation, complexation with PDMA still occurs in dioxane. This observation calls for a reexamination of the requirement of a long sequence of uninterrupted bonding sites as a prerequisite for complexation. Fourier transform infrared spectroscopy and ^{13}C NMR were used to study the hydrogen bonding interaction in blends and complexes.

Introduction

In a previous publication, mutual precipitation between poly(ethyloxazoline) and a phenol–formaldehyde resin was observed when acetone solutions of the two materials were mixed.[1] The precipitate contained about 56 mol % of the former, corresponding to a molar ratio of 4:3 of the interacting units. The glass transition temperature of the precipitate was found to be higher than that of either component polymer and also higher than the value of a solvent-cast blend film of the same composition.

The driving force for the complexation process is the cooperative formation of hydrogen bonds between acid and base groups. It has been reported that a minimum chain length, L_C of the interacting polymers is required for the formation of a stable complex.[2,3] Since the phenolic resin used in the earlier study is an oligomer containing only 10 repeating units, the critical length cannot be very large in this system.

The present study was undertaken to investigate complexation in related systems in order to gain further understanding of the glass transition temperature characteristics and the critical length requirement. In the first part of this study, the same phenolic resin and its *p*-methoxy-substituted derivative were used, but the high molecular weight component was chosen to be poly(*N*,*N*-dimethylacrylamide) which was isomeric with poly(ethyloxazoline). In the second part, the hydroxyl groups of the phenolic resin was partially converted to ethers to reduce the density of the proton-donating groups in the chain. The minimum number of hydroxyl groups required to cause mutual precipitation with poly(*N*,*N*-dimethylacrylamide) (PDMA) was determined. The properties of the complexes were compared with those of the blend films prepared from hydrogen bond breaking solvents.

Experimental Section

Materials. Phenol–formaldehyde resins were synthesized with calcium hydroxide as catalyst for the condensation reaction.[4] The use of divalent calcium ion as catalyst resulted in methylene linkages at the ortho positions only. The molecular weight of the poly[(1-hydroxy-2,6-phenylene)methylene] (PHMP) resin prepared by this procedure was determined by vapor phase osmometry to be about 1000. Substituted PHMP resin containing *p*-methoxy groups was synthesized from *p*-methoxyphenol by the same procedure and the molecular weight was about 1000–1100. PHMP was also modified to reduce the number of hydroxyl groups in the chain. This was accomplished by reaction with methyl iodide to convert a portion of the hydroxyl groups to the corresponding ethers. *N*,*N*-Dimethylacrylamide was polymerized at 70 °C for 3 h in 1,4-dioxane, using recrystallized azobis(isobutyronitrile). The intrinsic viscosity of the PDMA polymer measured at 25 °C in methanol was 0.3 dL/g from which the molecular weight was estimated as 5.6×10^4.

Preparation of Blend Films and Complexes. Polymer complexation was studied by mixing solutions containing 0.005 g of polymer per milliliter of solvent. The precipitates formed upon mixing were separated from the solution by centrifugation (if needed) and filtration, washed twice with solvent, and then dried in vacuum at 110 °C to constant weight. The content of poly(*N*,*N*-dimethylacrylamide) in each complex was determined by element analysis. The complexes were ground into powders for determination of glass transition temperatures.

Films of polymer blends were prepared by solution casting. Solvent mixtures of dichloroethane (61.5% by volume), acetonitrile (15.4%), and triethylamine (7.7%) were employed. Each film was vaccum dried at a temperature of at least 20 °C above its estimated glass transition temperature.

Determination of Glass Transition Temperature. The glass transition temperatures of the complexes and the blend films were determined by differential scanning calorimetry with the use of a thermal analysis instrument (Du Pont, Model 9900). Sample size was between 7 and 10 mg. Prior to the DSC measurement, each specimen was preheated to 140 °C and maintained at that temperature for 20 min. After cooling to 30 °C, a heating rate of 10 °C/min was used for the thermal scan. This procedure was adopted to ensure the complete removal of the residual solvent in the specimen. Thermogravimetric analysis confirmed the effectiveness of the pretreatment in solvent removal. The glass transition temperature was taken as the onset (extrapolated) of the abrupt increase in the specific heat of the sample. The T_g values are reproducible to about ±1 °C.

Infrared Spectroscopy. Blend films were cast from solution onto a KBr window. After the film was dried at room temperature for 12 h and then at 110 °C in a vacuum oven for 72 h, the KBr window was mounted in a high-temperature cell in a Digilab FTS 60 Fourier transform infrared spectrometer. Two hundred scans were signal-averaged at a resolution of 2 cm^{-1}. Spectra were recorded upon heating and cooling at 20 °C steps and, in the case of annealing experiments, at different time intervals.

The carbonyl group stretching band of PDMA occurred in the region of 1680–1554 cm^{-1} with maximum absorption at 1646 cm^{-1}. Upon mixing with PHMP resins, the overlapping peaks caused a broadening of the absorption band. After the absorption due to PHMP was subtracted from the spectra of the blend, the carbonyl band could be further resolved into a "free" carbonyl peak at 1646 cm^{-1} and a "bonded" carbonyl peak at 1608 cm^{-1}. The ratio of the area of the bonded carbonyl absorption, A_b, to the total area, A_t, is used here as the index for the extent of

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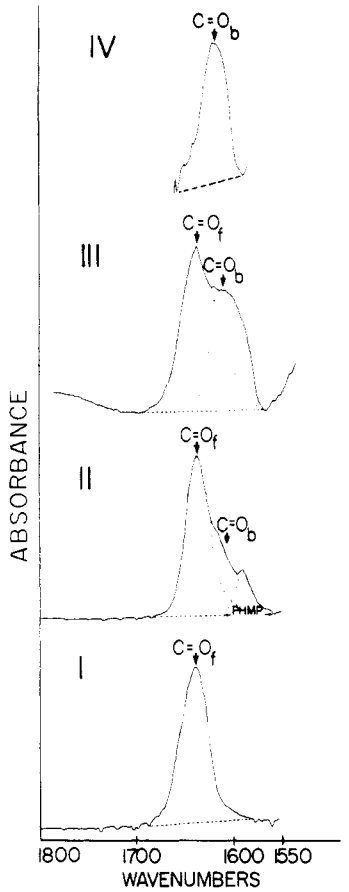

Figure 1. FTIR spectra of carbonyl region of (I) PDMA and (II) PDMA/PHMP (50/50 by weight) blend at 40 °C; (III) spectra obtained by subtracting PHMP absorption from (II) (expanded scale); (IV) hydrogen bonded carbonyl band obtained by subtracting (III) from (I).

hydrogen bonding. The fraction of bonded carbonyl can be calculated from the area ratio provided the conversion factor is known. For example, the conversion factor for the hydrogen-bonded carbonyl in an ester group was determined by Coleman and co-workers to be 1.5–1.6.[5] But the data obtained in our experiments showed a large scatter of the calculated conversion factors ranging from 1.0 to 1.5 due to the double-subtraction procedure. Typical results are shown in Figure 1. For this reason, only the results that can be represented by a conversion factor of 1.3 ± 0.1 are used, and we shall confine ourselves to the use of the area ratio in the ensuing discussion.

Nuclear Magnetic Resonance. ^{13}C CP/MAS NMR Spectra were recorded at 50 MHz with an IBM WP-200SY spectrometer equipped with a solid accessory for cross polarization and high-powered decoupling. A cylindrical double air bearing MAS probe from Doty Scientific Co. was used. Rotors with a sample volume of 0.36 cm^3 made of Al_2O_3 were routinely spun at 4 kHz. A constant time of 2 ms was used. The number of acquisitions ranged from 500 to 4000 with 2K data points zero filled to 4K. Delay time between acquisitions was 3 s. Chemical shift calibration was based on the methyl carbon (31 ppm) of p-di-*tert*-butylbenzene. Spectra subtractions were carried out with weighing factors determined by trial end error.

^1H NMR of *O*-methyl-PHMP was measured with the use of a Varian EM 390 spectrometer at 90 MHz to determine the degree of methylation. Deuterated acetone was used as solvent and tetramethylsilane as the internal standard.

Results and Discussions

Compositions of the Complexes. Complexation experiments were carried out in acetone, dioxane, and ethyl acetate solutions. The three solvents were chosen because the solubilities of both PHMP and PDMA could be arranged in the same order: acetone > dioxane > ethyl acetate. The solubilities of PHMP were determined to be about 8, 6, and 4 g per 100 g of solvent and the values for PDMA were about 4.5, 4, and 1 g/100 g at 28 °C. In terms of their affinities as hydrogen bond acceptors, however, dioxane was the most powerful, as evidenced by a large shift in the "free" hydroxyl stretching frequency of phenol from 3640 to 3322 cm^{-1}. The frequency was shifted to 3405 cm^{-1} in acetone and to 3453 cm^{-1} in ethyl acetate. These values are to be compared with the frequency shift to about 3300 cm^{-1} by *N,N*-dimethylacetamide, a model for PDMA. According to the enthalpy–frequency shift relationship,[6,7] PDMA is a stronger base than the solvents.

Table I
PHMP/PDMA Complex

sample	solvent	mol % PDMA in feed	complex: yield, wt %	complex: mol % PDMA	T_g, °C
1	acetone	25	50	45	143
2	acetone	33	62	44	153
3	acetone	50	77	56	136
4	acetone	66	64	61	136
5	acetone	75	53	66	135
6	dioxane	25	58	40	136
7	dioxane	33	67	49	138
8	dioxane	50	78	57	139
9	dioxane	66	63	60	136
10	dioxane	75	41	64	136
11	ethyl acetate	25	59	37	159
12	ethyl acetate	33	68	46	152
13	ethyl acetate	50	84	50	144
14	ethyl acetate	66	91	64	151
15	ethyl acetate	75	95	74	152

The solubilities of *p*-methoxy-PHMP were 10, 8, and 12 g per 100 g of solvent in acetone, dioxane, and ethyl acetate. *O*-methyl(40%)-PHMP was soluble in dioxane but not in acetone or ethyl acetate.

The yields of mutual precipitation of PHMP and PDMA from the three solvents and the compositions of the complexes are compiled in Table I. Material balance calculations revealed that for solution mixtures rich in PHMP content, nearly all the PDMA (83–100%) precipitated; but for solutions poor in PHMP content, the latter was completely consumed in complexation only from ethyl acetate (samples 14 and 15) but not from acetone or dioxane. Obviously, precipitation was more favored in a poor solvent. For solutions containing equimolar quantities of the two components, neither was completely consumed in precipitation.

The compositions of the complexes corresponded in most cases to simple molar ratios of PDMA to PHMP, for example, 3:5, 2:3, 4:5, 1:1, 4:3, 3:2, 2:1, and 3:1. When the mole fraction of PDMA in the complex, F_1, was plotted against the mole fraction, f_1, of PDMA in the solution mixture, in analogy with a copolymer composition plot, certain patterns seemed to emerge, Figure 2. There were three azeotropes, 1:1, 2:1, and 3:1, all from ethyl acetate. For the other precipitates, F_1 was always greater than f_1 when the latter was 0.5 or less. But the relationship was reversed when f_1 exceeded 0.5.

Sample 3 is of particular interesting because it bears comparison with the result of an earlier study on PHMP/poly(ethyloxazoline), the latter polymer being an isomer of PDMA. Indeed, the same complex composition was obtained.

Mutual precipitation of *p*-methoxy-PHMP and PDMA produced different results (Table II). The compositions of the complexes corresponded to molar ratios of 3:4, 1:1, 3:2, 2:1, 3:1, and 4:1. Samples 20, 25, and 30 had composition close to that of the azeotropes, about 3:1. But the rest of the complexes had F_1 values larger than the cor-

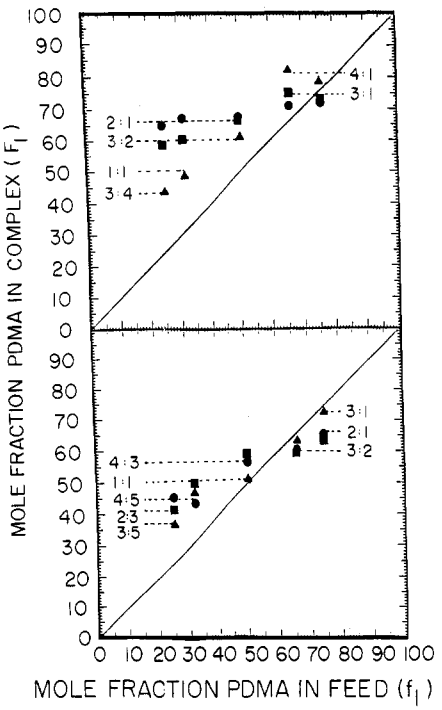

Figure 2. Relationship between feed composition and complex composition: upper diagram, PDMA/P-methoxy PHMP; lower diagram, PDMA/PHMP. (●) Acetone; (▲) ethyl acetate; (■) 1,4-dioxane.

Table II
***p*-Methoxy-PHMP/PDMA Complex**

sample	solvent	mol % PDMA in feed	complex yield, wt %	complex mol % PDMA	T_g, °C
16	acetone	25	34	65	136
17	acetone	33	46	67	138
18	acetone	50	70	67	143
19	acetone	66	86	72	137
20	acetone	75	91	72	136
21	dioxane	25	32	58	139
22	dioxane	33	45	60	140
23	dioxane	50	63	67	126
24	dioxane	66	86	75	137
25	dioxane	75	73	74	140
26	ethyl acetate	25	32	43	127
27	ethyl acetate	33	42	48	128
28	ethyl acetate	50	72	60	136
29	ethyl acetate	66	77	82	130
30	ethyl acetate	75	97	78	128

responding feed compositions (Figure 2). The *p*-methoxy group, being also a hydrogen bond acceptor, apparently alters the driving force and stoichiometry of complexation.

Partial conversion of the hydroxyl groups in PHMP to methyl ether groups reduced the density of hydrogen bond donors in the chain. Up to a conversion of about 40%, mutual precipitation still occurred in dioxane. However, no precipitation was observed when the conversion was larger. For a feed composition of $f_1 = 0.50$ in PDMA/*O*-methyl(40%)-PHMP/dioxane system, the yield of the precipitate was 30% and F_1 was 0.60.

The cooperative interaction effect on interpolymer complexation was frequently discussed in terms of a critical sequence length L_c required for the formation of a stable complex. In a study of interpolymer association between polyacrylic acid and poly(oxyethylene), Iliopoulos and Audebert[8a,b] and Kabanov et al.[8c] reported that a large number of vicinal acid units in the PAA chain was required for complexation. However, Morawetz et al.[8d,e] were the first to point out the shortcomings of such a requirement,

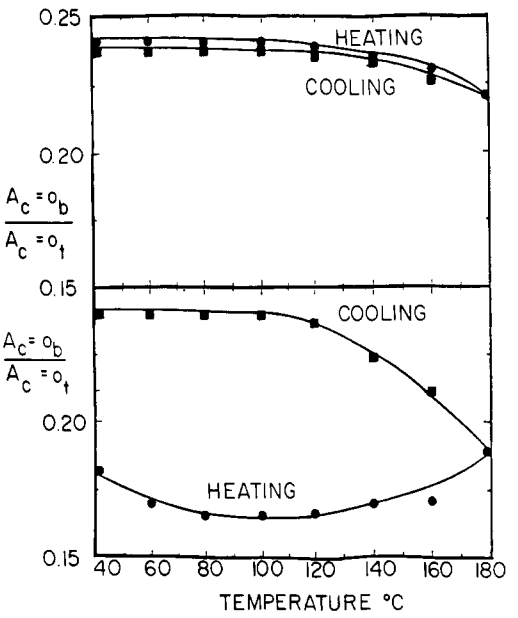

Figure 3. Glass transitions temperatures of blends of PDMA with PHMP and *p*-methoxy-PHMP: upper diagram, PDMA/*p*-methoxy-PHMP; lower diagram, PDMA/PHMP.

on both experimental and theoretical grounds. The results of this study and those reported for poly(ethyloxazoline)/poly(acrylic acid-*co*-styrene) likewise indicate that a much shorter uninterrupted sequence is sufficient to cause mutual precipitation in certain systems. A reexamination of the requirement of a large number of contiguous interacting groups arranged in perfect array toward each other for stable complexes appears to be in order.

Glass Transition Temperatures. The glass transition temperature of PDMA was 118 °C and that of PHMP, 84 °C. The precipitates all had glass temperatures higher than the component T_g's (Table I). The high values could be attributed to hydrogen bonds acting as physical cross-links. Complexes obtained from acetone and dioxane generally had comparable T_g's, but the precipitates from ethyl acetate had higher values. However, we did not detect a clear trend of the dependence of T_g on composition.

When *p*-methoxy-PHMP, with a T_g of 80 °C, was used, the T_g data of the complexes obtained from acetone and dioxane were similar to those of PHMP complexes. But the precipitates from ethyl acetate had significantly lower T_g values when compared with PHMP complexes (Table II).

O-Methyl(40%)-PHMP has a T_g of 36 °C. The complex obtained from dioxane solution had a T_g of 134 °C. Apparently a high glass temperature can still be obtained even when the number of hydrogen bond donors in the chain is reduced to almost half.

Blend films of PDMA/PHMP and PDMA/*p*-methoxy-PHMP were cast from mixed solvents (see Experimental Section). The T_g's of these blends were either equal to or higher than the calculated weight-average values (Figure 3). In many other hydrogen-bonded blends, high T_g values have also been observed, and our data are consistent with the results of earlier studies.[9-11] However, in comparison with complexes of the same compositions, the blend T_g's are still low. In an attempt to investigate whether the T_g of a blend would be affected by annealing, we heated each blend film to 180 °C for 3 h. The thermal treatment resulted in an increase in T_g for each blend as shown in Tables III and IV.

Table III
Glass Transition Temperatures of PDMA/PHMP Blends

sample	comp, % PDMA wt	comp, % PDMA mol	T_g, °C	T_g, °C, after anneal 180 °C/3 h
31	0	0	84	84
32	10	11	98	105
33	20	21	102	112
34	30	31	99	106
35	40	41	97	134
36	50	52	101	129
37	60	61	108	138
38	70	71	111	121
39	80	81	113	123
40	90	91	116	125
41	100	100	118	118

Table IV
Glass Transition Temperatures of *p*-Methoxy-PHMP/PDMA Blends

sample	comp, % PDMA wt	comp, % PDMA mol	T_g, °C	T_g, °C, after anneal 180 °C/3 h
42	0	0	80	80
43	10	13	90	93
44	20	26	101	119
45	30	37	107	114
46	40	48	113	119
47	50	58	107	120
48	60	67	107	125
49	70	76	113	120
50	80	84	116	129
51	90	93	117	124
52	100	100	118	118

A second method of altering the T_g of the blend was exposure to solvent. A 1:1 blend film of PDMA/PHMP was exposed to the vapor of ethyl acetate in a closed jar at ambient temperature for a period of 20 days and subsequently dried by the usual procedure. The T_g of the film was found to increase from the original value of 101 to 119 °C. If the film was immersed in ethyl acetate liquid which swelled but did not dissolve the film, the T_g became 128 °C.

Extent of Hydrogen Bonding. An intuitive explanation of the increase in T_g caused by annealing was that the extent of hydrogen bonding had increased during the annealing process. In order to verify our hypothesis, we carried out infrared spectroscopic measurements in the carbonyl group absorption region of 1680–1554 cm^{-1}. The ratio of the peak area of the hydrogen-bonded carbonyl to the area of the total absorption, A_b/A_t, was determined for a 50/50 (mol %) PHMP-PDMA blend. The ratio indeed was found to increase after annealing. We then conducted measurements at 20 °C intervals in successive heating and cooling cycles. The fraction of bonded carbonyl initially decreased upon heating from 40 to 100 °C but then increased from 100 to 180 °C (Figure 4). The shape of the heating curve was the opposite to what one would expect of increasing dissociation of hydrogen bonds at high temperatures as had been found in numerous earlier investigations.[5,10] The bond fraction increased in magnitude upon cooling from 180 °C and the cooling curve had the normal shape associated with the reestablishment of hydrogen bonds as temperature was lowered. After the temperature was returned to 40 °C, the second heating and cooling cycle induced only minor changes in A_b/A_t ratios. The third thermal cycle reproduced the results of the second cycle. The lare discrepancies in the A_b/A_t ratios during the first thermal cycle were highly suggestive of spatial rearrangement of the interacting groups in the

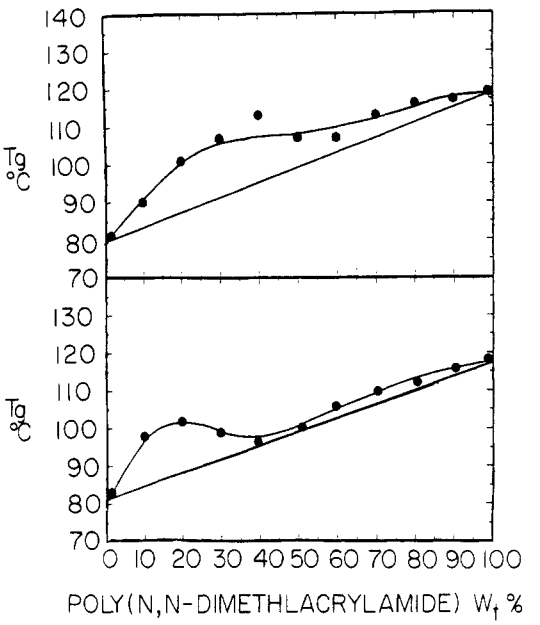

Figure 4. Fraction of bonded carbonyl group in a 1:1 PDMA/PHMP blend as a function of temperature: upper diagram, second heating and cooling cycle; lower diagram, first cycle. (●) Heating; (■) cooling.

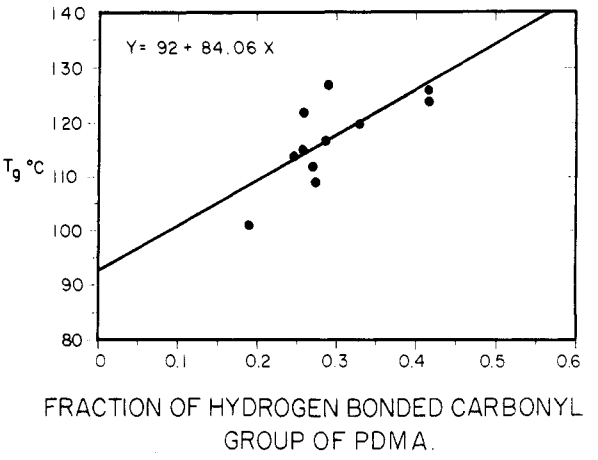

Figure 5. Fraction of bonded carbonyl group in a 1:1 PDMA/PHMP blend at different annealing temperatures as a function of time.

blend during heating to allow additional hydrogen bonding. The A_b/A_t ratios in the first heating curve could be viewed as representing a combination of two opposing effects: the normal dissociation effect which decreased hydrogen bonding when temperature was raised and a rearrangement effect which promoted hydrogen bonding. In support of this interpretation we noted that the rearrangement effect became dominant above 100 °C, the T_g of the blend.

We also noticed that during the second thermal cycle the bonded fraction did not decrease with temperature until the T_g of the annealed blend, now at 128 °C, was neared. The temperature coefficient of the bonded fraction above T_g appeared to be smaller than that found for PHMP–poly(methyl acrylate)[10] but comparable to that obtained for poly(4-hydroxystyrene)–poly(vinyl acetate).[12]

Additional spectroscopic studies were carried out by measuring the fraction of bonded carbonyl as a function of time at a given temperature. The results shown in Figure 5 indicated that there were only minor changes in the magnitude of A_b/A_t with time once the temperature of the experiment had been reached. (The time required to reach the desired temperature was between 5 and 15

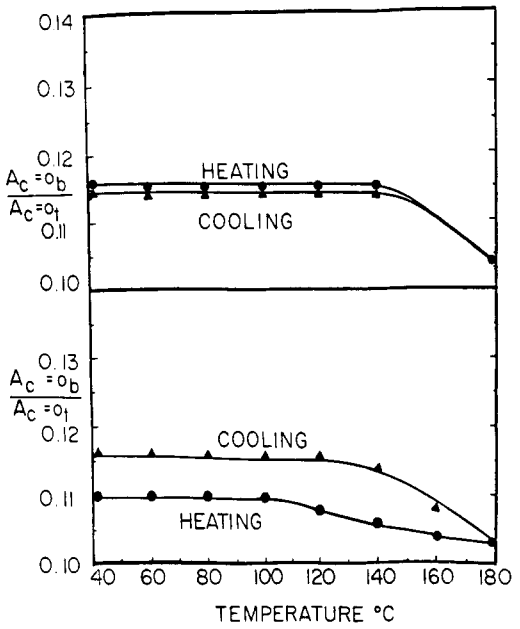

Figure 6. Correlation between glass transition temperature and fraction of hydrogen-bonded carbonyl group in a 1:1 PDMA/PHMP blend, after various thermal treatment.

min.) The A_b/A_t values at first decreased when the temperature was raised from 40 to 130 °C but increased slightly between 130 and 150 °C. At the latter temperature, the A_b/A_t ratio nearly regained the value at 40 °C. A large increase in the magnitude of A_b/A_t was seen between 150 and 160 °C and between 160 and 170 °C. The values at 180 °C were only marginally higher. These results are consistent with the findings depicted in Figure 4.

Although it is gratifying that the increase in T_g by annealing indeed goes hand in hand with more extensive hydrogen bonding, we seek to establish a quantitative correlation between the two properties and have therefore undertaken the following experiments. Ten pieces of 50/50 blend films were annealed at different temperature–time conditions and their T_g's determined. The fraction of bonded carbonyl for each sample was determined after it was subjected to the specified annealing condition plus the thermal history incurred in the DSC measurement, including preheating, cooling, and the final thermal scan for T_g determination. The A_b/A_t value at T_g was recorded in each case and converted to the fraction of bonded carbonyl by using the conversion factor of 1.3 and the relation $(C{=}O)_b/(C{=}O)_t = 1.3A_b/(A_f + 1.3A_b)$. The T_g values and the corresponding bonded fractions measured by the above procedure were plotted in Figure 6. A linear dependence of T_g on the bonded fraction was indicated by the data although admittedly only a narrow range of the magnitude of either parameter was accessible. But if the correlation is accepted with this reservation in mind, an extrapolation of the straight line to zero bonded carbonyl gives a T_g of 92 °C, which may be interpreted as the value for a hypothetical blend with no interpolymer hydrogen bonding. On the other hand, extrapolation to the T_g of 144 °C for a 1:1 complex from ethyl acetate yields a value of 0.63 for the bonded fraction, indicating a high efficiency of hydrogen bonding in the complex.

The temperature dependence of the fraction of bonded carbonyl in a 2/1 PDMA/*p*-methoxy-PHMP blend had different characteristics (Figure 7). In the first thermal cycle, the bond fraction did not change upon heating until the temperature reached 100 °C and then decreased only slightly between 100 and 180 °C. Upon cooling, the A_b/A_t

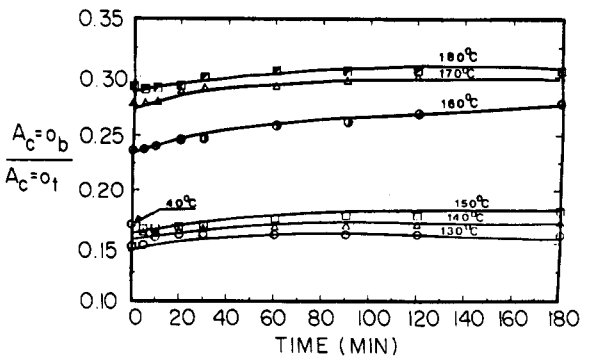

Figure 7. Fraction of bonded carbonyl group in a 2:1 PDMA/*p*-methoxy-PHMP blend as a function of temperature: upper diagram, second heating and cooling cycle; lower diagram, first cycle. (●) Heating; (▲) cooling.

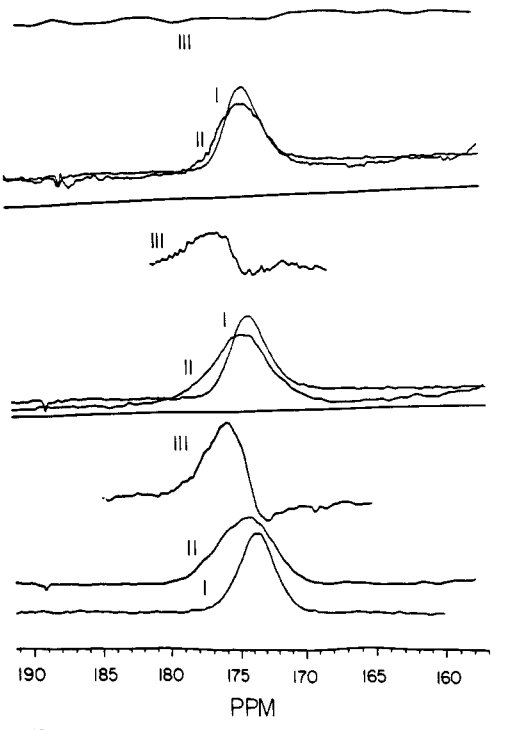

Figure 8. ^{13}C NMR chemical shift of the bonded carbonyl group. Upper diagram, blend from PDMA/PHMP in 1:1 mol: (I) PDMA carbonyl group band; (II) carbonyl group band of blend; (III) (II) – (I). Middle diagram, annealed blend from PDMA/PHMP in 1:1 mol: (I) PDMA carbonyl group band; (II) carbonyl group band of annealed blend; (III) (II) – (I). Lower diagram, complex from PDMA/PHMP in 1:1 mol: (I) PDMA carbonyl group band; (II) carbonyl group band of complex; (III) (II) – (I).

ratios were again higher. During the second thermal cycle, the bond formation remained constant until 140 °C which was approximately 15 °C above the T_g of the annealed blend. The ratio began to decrease at higher temperatures, as expected from the more facile dissociation of hydrogen bonds above T_g. Although the change in the bond fraction with temperature is minor compared with that of PHMP blends, annealing at 180 °C still resulted in an increase in T_g, as shown in Table IV. A different relationship between T_g and A_b/A_t is probably operative in this blend.

Nuclear Magnetic Resonance. Since the precipitates were not suitable for infrared measurements, we carried out several preliminary experiments to detect evidence of bonded carbonyl from NMR chemical shifts. The broadening of the carbonyl absorption was used as an indication for hydrogen bonding (Figure 8). The bonded carbonyl is assigned a chemical shift of 177 ppm, a 3 ppm shift from the free carbonyl absorption at 174 ppm. A shift of the

same magnitude was found in complexes of poly(4-hydroxystyrene)/PDMA. It is readily seen from Figure 8 that the fraction of bonded carbonyl in a 1:1 PDMA/PHMP blend film is very small. The bond fraction is significant in the annealed blend but has an even larger value in the complex formed from ethyl acetate. These findings are qualitatively in agreement with the conclusions drawn from infrared and T_g measurements (Figure 6).

Conclusion

Mutual precipitation occurs between PDMA and PHMP from acetone, dioxane, and ethyl acetate solutions. The compositions of the complexes can be represented in most cases by simple molar ratios of the components. The glass transition temperatures of the complexes are higher than the T_g value of either component.

PDMA and *p*-methoxy-PHMP also form complexes. Again the compositions of the complexes can be represented by simple molar ratios. The glass transition temperatures of the complexes are also higher than the component T_g values.

When 40% of the hydroxyl groups in PHMP were methylated, mutual precipitation with PDMA still occurred in dioxane. This observation calls for a reexamination of the requirement of a long sequence of uninterrupted bonding sites in a chain as a prerequisite for complexation.

Blend films cast from hydrogen bond breaking solvents have lower T_g values than the corresponding complexes of the same compositions. But the glass transition temperatures of the blends can be raised by thermal treatment during which a concomitant change in the fraction of bonded carbonyl groups in PDMA occurs. A correlation between T_g and the bonded carbonyl group is suggested. It is estimated from the correlation that at least 53% of the carbonyl group are hydrogen bonded in a 1:1 complex of PDMA/PHMP having a T_g of 144 °C.

^{13}C CP/MAS NMR experiments showed a chemical shift of 3 ppm for the bonded carbonyl absorption. The fractions of bonded carbonyl increase in the order blend < annealed blend < complex, in agreement with T_g data.

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Registry No. PDMA, 26793-34-0; (phenol)(formaldehyde) (copolymer), 9003-35-4; (phenol)(*p*-methoxyphenol) (copolymer), 38639-99-5.

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Rotational Relaxation Time and Conformational Transition of Poly(acrylic acid) As Studied by the Conductance Stopped-Flow Technique

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ABSTRACT: The rotational relaxation time (τ_r) of poly(acrylic acid) (HPAA) in aqueous media of various pH values has been determined by the conductance stopped-flow technique. The effective length of a single chain may be evaluated from the relaxation time, τ_r. The conformation of the macroion chain is found to be highly stretched in the presence of added NaOH. The deionized HPAA chain at α (degree of neutralization) = 0 is stretched by the electrostatic intersegment repulsive interaction and the elongated Debye screening length around the macroions. The chain shrinks significantly with decreasing α in the region of negative α.

Introduction

In preceding papers,[1-3] the author has used the conductance stopped-flow (CSF) and spectrophotometric stopped-flow (SP-SF) techniques to obtain information on the rotational relaxation times and rotational diffusion times of anisotropic macroions such as ellipsoidal colloids of tungstic acid, deoxyribonucleic acid, and sodium poly(styrenesulfonate) in aqueous solution. The rotational relaxation processes of the conductance anisotropy were first discussed for ionic detergents,[4,5] polyphosphates,[6-9] graphitic acid colloids,[5,10] deoxyribonucleic acid,[10] and poly(methacrylic acid)[11] by using the Couette apparatus. In the present paper the rotational diffusion times of poly(acrylic acid) (HPAA) are reported in salt-free ("deionized") solution and in the presence of NaOH or HCl, from which the effective rod length has been evaluated.

Anisotropic molecules are expected to orient themselves along stream lines during continuous flow. When the solution flow is stopped, the molecules revert to a random orientation by a Brownian rotation. The translational motion is not significant in the stopped-flow method, since the flow of the solvent molecules have stopped completely by the time the observation is started. The macroions might be deformed by the flow field, but we assume that at the moment the flow is stopped, the macromolecules

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