

Miscibility and Complexation Behavior of Poly(cyanomethyl methacrylate) and Poly(2-cyanoethyl methacrylate) with Tertiary Amide Polymers

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SYNOPSIS

The miscibility and complexation behavior of poly(cyanomethyl methacrylate) (PCYMMA) and poly(2-cyanoethyl methacrylate) (PCYEMA) with various tertiary amide polymers was studied. PCYMMA and PCYEMA form interpolymer complexes with poly(*N*-methyl-*N*-vinylacetamide) (PMVAc) or poly(*N*-vinyl-2-pyrrolidone) (PVP) in tetrahydrofuran (THF) solutions. PCYMMA also forms complexes with poly(*N,N*-dimethylacrylamide) (PDMA) in THF solutions. However, PCYEMA does not form complexes with PDMA in THF solutions, but the THF-cast blends are miscible over the entire composition range. Both PCYMMA and PCYEMA do not form complexes with poly(2-ethyl-2-oxazoline) (PEOx) in THF solutions and are only miscible with PEOx when the blend contains greater than 60 wt % PCYMMA or 80 wt % PCYEMA. On the other hand, both PCYMMA and PCYEMA do not form complexes with PMVAc, PVP, or PDMA in *N,N*-dimethylformamide (DMF) solutions. The compositions of the complexes consist of simple mole ratios of the component polymers, and the glass-transition temperatures of the complexes are higher than those of the DMF-cast blends of similar compositions. Fourier-transform infrared spectroscopy provides further evidence on the miscibility behavior through changes in the amide carbonyl absorption bands of each tertiary amide polymer in the blends as well as in the cyano absorption band of PCYEMA. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It has been established that the formation of a miscible blend between two chemically dissimilar polymers requires specific intermolecular interactions between them. When the specific interactions are sufficiently strong, such as those involving hydrogen-bonding interactions and coulombic interactions between oppositely charged polymers, the two polymers may form interpolymer complexes.^{1,2} One characteristic of interpolymer complexes is that their glass-transition temperatures (T_g s) are usually higher than the weight-average T_g values of the component polymers.

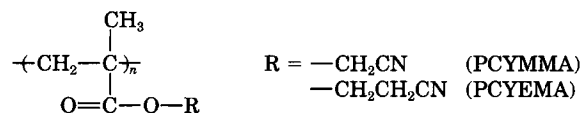
Tertiary amide polymers such as poly(*N*-vinyl-2-pyrrolidone) (PVP), poly(*N,N*-dimethylacrylam-

ide) (PDMA), poly(*N*-methyl-*N*-vinylacetamide) (PMVAc), and poly(2-ethyl-2-oxazoline) (PEOx) can form interpolymer complexes with polymers containing acid or hydroxyl groups. Some examples include PVP/poly(acrylic acid) (PAA),¹ PEOx/PAA,^{3,4} PDMA/poly(*p*-vinylphenol) (PVPh),⁵ and PMVAc/poly(styrene-*co*-allyl alcohol) (SAA)⁶ complexes. Our recent studies show that the abilities of tertiary amide polymers to form complexes with hydroxyl-containing polymers are in the order of PMVAc > PDMA > PEOx.^{7,8}

We have recently reported the miscibility behavior of two cyano-containing polymethacrylates, namely, poly(cyanomethyl methacrylate) (PCYMMA) and poly(2-cyanoethyl methacrylate) (PCYEMA).^{9,10} We now report the miscibility of PCYMMA and PCYEMA with tertiary amide polymers. It will be shown that both PCYMMA and PCYEMA can form interpolymer complexes with PVP or PMVAc, but not with PEOx. In addition,

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PCYMMA also forms complexes with PDMA. To our knowledge, there are no previous reports on interpolymer complexes involving cyano-containing polymers.



EXPERIMENTAL

Materials

PCYMMA and PCYEMA were prepared as described previously.^{9,10} The number-average (M_n) and weight-average (M_w) molecular weights of PCYMMA determined by gel permeation chromatography (GPC; polystyrene standards, tetrahydrofuran, THF) were 38.6 and 59.9 kg/mol, respectively. The intrinsic viscosity $[\eta]$ of PCYEMA was 0.55 dL g⁻¹ in *N,N*-dimethylformamide (DMF) at 23°C. *N*-methyl-*N*-vinylacetamide and *N,N*-dimethylacrylamide were purchased from Fluka AG. Both monomers were purified through vacuum distillation and each was separately polymerized in 1,4-dioxane at 80°C for 4 h using azobisisobutyronitrile (AIBN) as initiator. The polymers PMVAc and PDMA were subsequently obtained through precipitation in *n*-hexane. PVP and PEOx were obtained commercially. The molecular weights and T_g s of these tertiary amide polymers are shown in Table I.

Polymer Complexes

THF solutions (2.5 wt %) of PCYMMA and tertiary amide polymers were separately prepared. Appropriate volumes of the solutions were mixed so that the weight ratios of PCYMMA and the tertiary

amide polymers correspond to 1 : 1, 1 : 3, 1 : 9, 3 : 1, and 9 : 1. The complexes formed were then collected through centrifugation and washed twice with THF. The residual filtrates and washings were also collected and cast as blends (thereafter denoted as residual blends) in weighed aluminum pans, and left to evaporate for 1–2 days. Both the complexes and residual blends were subsequently dried at 90°C *in vacuo* for at least 4 days. For the PCYEMA system, THF/acetone (9/1) solution was used as the solvent to facilitate the dissolution of PCYEMA.

Complex Composition Determination

Because nitrogen is present in PCYMMA, PCYEMA, as well as in the tertiary amide polymers, the determination of complex composition based on elemental analysis of nitrogen would not be feasible. However, the problem was overcome by taking the proton nuclear magnetic resonance (¹H-NMR) spectrum of each weighed complex sample together with an internal standard of a fixed known mass, and monitoring the intensity of the methylene proton signal of —CH₂CN of PCYMMA or PCYEMA. The internal standard chosen was chloroacetonitrile whose methylene proton signal at 4.72 ppm does not interfere with the methylene proton signal of PCYMMA at 4.95 ppm and PCYEMA at 4.09 ppm. To determine the composition of the complex, a calibration graph was first established by taking the ¹H-NMR spectra of three known masses of PCYMMA (or PCYEMA) in deuterated-dimethylsulfoxide, each containing the same mass of the internal standard. The three masses were selected to include all of the possible known masses of PCYMMA present in the complexes. The intensities of the methylene proton signal of the —CH₂CN group of PCYMMA as well as those of the internal standard were then monitored for each sample. A calibration graph of mass ratio (ClCH₂CN/PCYMMA) against intensity ratio of the methylene

Table I Characteristics of Tertiary Amide Polymers

Polymer	Abbreviation	Source	M_w (kg/Mol)	M_n (kg/Mol)	T_g (°C)
Poly(<i>N,N</i> -dimethylacrylamide)	PDMA	Author's Laboratory	20	12	112
Poly(<i>N</i> -methyl- <i>N</i> -vinylacetamide)	PMVAc	Author's Laboratory	3.7	3.3	133
Poly(<i>N</i> -vinyl-2-pyrrolidone)	PVP	Scientific Polymer Products	40	—	160
Poly(2-ethyl-2-oxazoline)	PEOx	Dow Chemical Co.	200	—	50
Poly(cyanomethyl methacrylate)	PCYMMA	Author's Laboratory	60	39	97
Poly(2-cyanoethyl methacrylate)	PCYEMA	Author's Laboratory	$[\eta] = 0.55 \text{ dL g}^{-1}$ 23°C in DMF	—	89

proton ($\text{ClCH}_2\text{CN}/\text{PCYMMA}$) was then plotted (Fig. 1). Thereafter, the $^1\text{H-NMR}$ spectra of the weighed complex samples, each containing the same fixed mass of the internal standard used for calibration, were taken and the intensity ratios of the methylene protons ($\text{ClCH}_2\text{CN}/\text{PCYMMA}$) were determined. The mass ratios were subsequently obtained from the calibration plot and the amount of PCYMMA present in each complex sample was thus calculated. A calibration plot for the $\text{ClCH}_2\text{CN}/\text{PCYEMA}$ system was similarly prepared. All the $^1\text{H-NMR}$ spectra were obtained with a Bruker AMX 500 NMR spectrometer.

Polymer Blends

For comparison purposes, blends of PCYMMA and PCYEMA with PDMA, PVP, and PMVAc in varying weight ratios were also prepared by solution casting from DMF where no complex formation was observed. The initial evaporation of DMF was done on a hot plate maintained at 100°C . Blends of PCYMMA and PCYEMA with PEOx were, however, prepared by casting from THF and THF/acetone (9/1), respectively. No complex formation was observed. The solvent was allowed to evaporate slowly over a period of 1–2 days at room temperature. All the blends were subsequently dried *in vacuo* at 90°C for at least 10 days.

T_g Measurements

The T_g of various samples were measured with a Perkin–Elmer DSC-4 differential scanning calorimeter using a heating rate of $20^\circ\text{C}/\text{min}$. The blend samples, as well as the polymer complexes, were subjected to a heat treatment at 130°C for 10 min prior to thermal characterization. The purpose was to remove any adsorbed moisture because the tertiary amide polymers are hygroscopic. The T_g value was taken as the initial onset of the change of slope in the DSC curve. The reported T_g is the average value based on the second and subsequent runs.

FTIR Studies

Infrared spectra were recorded on a Perkin–Elmer model 1725X spectrophotometer. A minimum of 64 scans at 2 cm^{-1} spectral resolution were averaged in all cases. Samples were prepared by casting 1% DMF solutions (w/v) of polymer blend directly onto KBr discs. The discs were heated at 90°C to enable DMF to evaporate slowly and were subsequently dried in a vacuum oven at 90°C for at least 4 days. The films thus obtained were thin enough to meet Lambert–Beer law requirements. All the scans were taken at 60°C using a Specac 21500 variable temperature cell connected to a Specac Eurotherm automatic temperature controller.

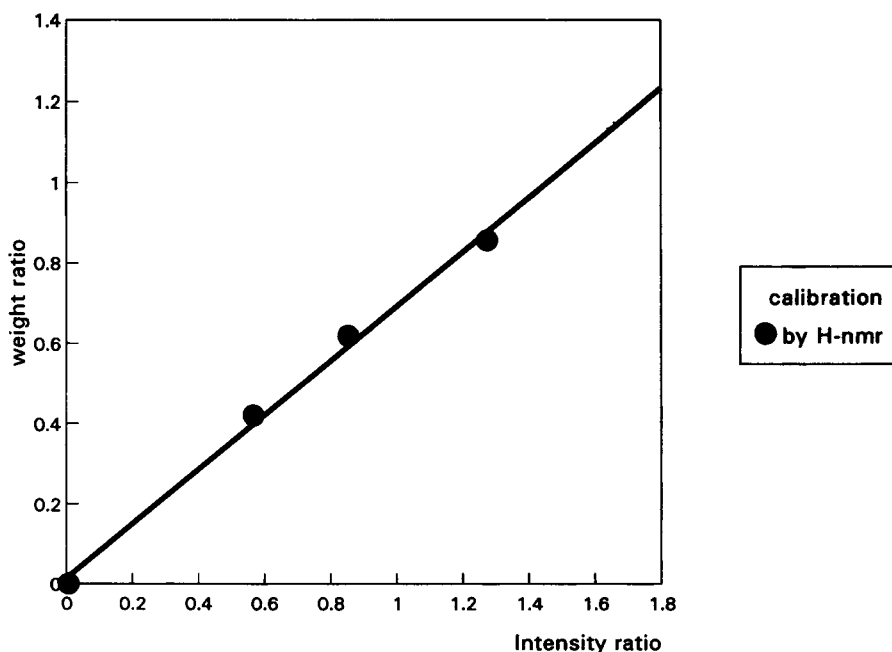


Figure 1 Calibration graph of $\text{ClCH}_2\text{CN}/\text{PCYMMA}$ weight ratio against intensity ratio of methylene protons in $\text{ClCH}_2\text{CN}/\text{PCYMMA}$ mixture.

Table II Characteristics of PCYMMA/PDMA Complexes

PDMA Content in Feed (Mol %)	Complex			Residual Blend		
	Yield (Wt %)	PDMA Content (Mol %)	T_g (°C)	Yield (Wt %)	PDMA Content (Mol %)	T_g (°C)
92 (90)*	26	68 (1 : 2) [†]	112	74	100	112
79 (75)	56	67 (1 : 2)	115	44	94	108
56 (50)	84	58 (2 : 3)	105	16	32	93
30 (25)	40	58 (2 : 3)	108	60	7	99
12 (10)	18	53 (1 : 1)	102	82	3	91

* Wt % PDMA in feed.

[†] Molar ratio of PCYMMA/PDMA.

RESULTS AND DISCUSSION

Complexation Behavior

PCYMMA forms interpolymer complexes with PDMA, PMVAc, or PVP in THF solutions while PCYEMA forms complexes with PMVAc or PVP but not with PDMA. However, both PCYMMA and PCYEMA do not form complexes with PEOx in THF solutions. The behavior is consistent with our earlier observation that PEOx has the poorest complexation ability among the four tertiary amide polymers.^{7,8}

The characteristics of various complexes and residual blends are tabulated in Tables II–VI. Several interesting points are noted. First, the yields of the complexes reach a maximum when nearly equal molar ratios of the two polymers are mixed. Second, the composition of the complex depends on the feed composition, but it can be expressed in simple molar ratio. Third, at a low PCYMMA or PCYEMA content in the feed, practically all of the cyano-containing polymethacrylates (PMAs) have been com-

plexed with the tertiary amide polymers, and the residual blends essentially contain only the tertiary amide polymers. Conversely, at a high PCYMMA or PCYEMA content, nearly all of the tertiary amide polymers have been complexed with the cyano-containing PMAs. In addition, calculations show that the sum of the amount of tertiary amide polymer in the complex and in the residual blend agrees well with the amount of the polymer in the initial feed, indicating the reliability of the determination of complex composition by NMR studies.

Thermal Characterization

It has been established that the nature of the solvent used can have a profound effect on the formation of interpolymer complexes.^{1,2} Complexation does not occur in a solvent that can effectively compete against interpolymer association and DMF is one of such solvents.^{3,6,7} Both PCYMMA and PCYEMA do not form complexes with PVP, PMVAc, or PDMA in DMF solutions.

Table III Characteristics of PCYMMA/PMVAc Complexes

PDMA Content in Feed (Mol %)	Complex			Residual Blend		
	Yield (Wt %)	PMVAc Content (Mol %)	T_g (°C)	Yield (Wt %)	PMVAc Content (Mol %)	T_g (°C)
92 (90)*	21	68 (1 : 2) [†]	128	79	100	126
79 (75)	59	69 (1 : 2)	127	41	96	130
56 (50)	75	63 (2 : 3)	124	25	19	92
30 (25)	50	51 (1 : 1)	122	50	7	93
12 (10)	19	51 (1 : 1)	122	81	2	97

* Wt % PMVAc in feed.

[†] Molar ratio of PCYMMA/PMVAc.

Table IV Characteristics of PCYMMA/PVP Complexes

PVP Content in Feed (Mol %)	Complex			Residual Blend		
	Yield (Wt %)	PVP Content (Mol %)	T_g (°C)	Yield (Wt %)	PVP Content (Mol %)	T_g (°C)
91 (90)*	42	79 (1 : 4) [†]	146	58	99	154
77 (75)	81	80 (1 : 4)	155	19	65	145
53 (50)	93	57 (4 : 5)	134	8	20	84
28 (25)	40	56 (4 : 5)	137	60	8	95
11 (10)	12	51 (1 : 1)	135	88	6	97

* Wt % PVP in feed.

[†] Molar ratio of PCYMMA/PVP.

All the blends of PCYMMA or PCYEMA with PVP, PDMA, or PMVAc cast from DMF had good optical clarity. Each of the blends had a single T_g , showing that PCYMMA and PCYEMA are miscible with the three tertiary amide polymers when cast from DMF.

Figure 2 shows the T_g -composition curve for PCYMMA/PDMA blends. The T_g values of the blends are lower than those weight-averaged values of the T_g s of the component polymers. One striking point is that the T_g values for blends rich in PCYMMA are lower than that of PCYMMA. The low T_g values may not arise from residual solvents in the blends as prolonged drying of blend samples failed to raise the T_g values. Saeki et al.¹¹ reported that the T_g values of miscible polystyrene (PS)/poly(α -methylstyrene) (P α MS) blends rich in PS were 20°C lower than that of PS, the low T_g component. Similar depressions of T_g values were also reported by Bui et al.¹² for miscible PS/P α MS blends and by Lin et al.⁴ for miscible PEO_x/PAA blends. The T_g -composition curves for PCYMMA/PMVAc

and PCYMMA/PVP blends show the same features as that of the PCYMMA/PDMA blends and are not shown here.

As shown in Figures 3–5, the depression of T_g values is not observed for the PCYEMA blends, although the T_g values of PCYEMA/PDMA and PCYEMA/PVP blends are also lower than the weight-averaged values of T_g s of the component polymers. Interestingly, for the PCYEMA/PMVAc blends, the T_g -composition curve shows a large positive deviation from the weight-averaged T_g values, which can be taken to indicate that PCYEMA interacts more strongly with PMVAc than with PVP or PDMA.

All the T_g -composition curves can be fitted by the Kwei equation¹³:

$$T_g = (w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2) + q w_1 w_2$$

where T_g , T_{g1} , T_{g2} are the glass-transition temperatures of the blend, polymer 1 and polymer 2, respectively; w_1 and w_2 are the weight fractions of

Table V Characteristics of PCYEMA/PVP Complexes

PVP Content in Feed (Mol %)	Complex			Residual Blend		
	Yield (Wt %)	PVP Content (Mol %)	T_g (°C)	Yield (Wt %)	PVP Content (Mol %)	T_g (°C)
93 (90)*	17	66 (1 : 2) [†]	129	83	99	143
81 (75)	58	66 (1 : 2)	128	41	95	143
58 (50)	78	51 (1 : 1)	124	22	74	124
32 (25)	43	49 (1 : 1)	122	58	13	84
14 (10)	18	39 (3 : 2)	125	82	8	86

* Wt % PVP in feed.

[†] Molar ratio PCYEMA/PVP.

Table VI Characteristics of PCYEMA/PMVAc Complexes

PMVAc Content in Feed (Mol %)	Complex			Residual Blend		
	Yield (Wt %)	PMVAc Content (Mol %)	T_g (°C)	Yield (Wt %)	PMVAc Content (Mol %)	T_g (°C)
92 (90)*	20	48 (1 : 1) [†]	142	80	99	131
79 (75)	40	49 (1 : 1)	136	60	98	130
56 (50)	79	59 (2 : 3)	138	21	49	115
30 (25)	57	27 (3 : 1)	124	43	38	109
12 (10)	28	25 (3 : 1)	121	72	11	82

* Wt % PMVAc in feed.

[†] Molar ratio of PCYEMA/PMVAc.

polymer 1 and polymer 2; and k and q are fitting parameters. The curves in Figures 2–5 were drawn using the appropriate k and q values.

For comparison purposes, the T_g values of various complexes obtained from THF solutions are also shown in Figures 2–5. It is apparent that a complex has a higher T_g value than a blend of similar composition. Similar observations have been reported for other systems.^{5,14,15}

As mentioned earlier, PCYMMA and PCYEMA do not form complexes with PEOx in THF solutions. DSC measurements on the THF-cast blends show that both PCYMMA and PCYEMA are miscible with PEOx only over certain composition ranges.

Figure 6 shows the DSC curves of various PCYMMA/PEOx blends. Miscibility is achieved when the blend contains more than 60 wt % of PCYMMA or more than 80 wt % of PCYEMA. The T_g -composition curves for these two blend systems are shown in Figures 7 and 8.

FTIR Characterization

The amide carbonyl absorption bands of the tertiary amide polymers span from 1700 to 1590 cm^{-1} and do not overlap with the carbonyl absorption band of PCYMMA at 1745 cm^{-1} and that of PCYEMA at 1732 cm^{-1} . Figure 9 shows the FTIR spectra in

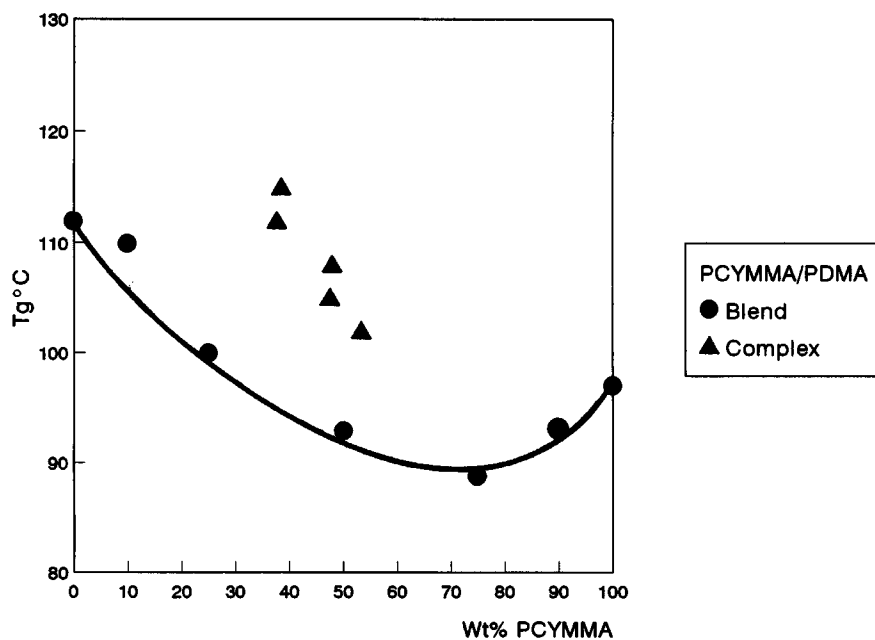


Figure 2 T_g -composition curve of PCYMMA/PDMA blends ($k = 1.2$, $q = -55$). (●) DMF-cast blend and (▲) complex.

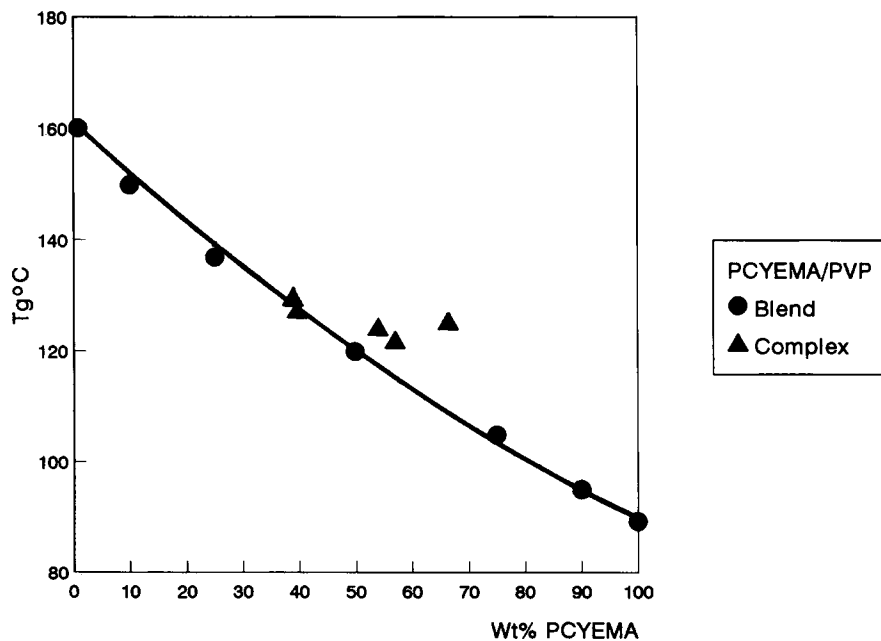


Figure 3 T_g -composition curve of PCYEMA/PVP blends ($k = 1.2$, $q = -28$). (●) DMF-cast blend and (▲) complex.

the amide carbonyl region of various PCYMMA/PVP blends. The addition of PCYMMA leads to the development of overlapping bands in the amide carbonyl region and the center of the band shifts to lower frequencies with increasing PCYMMA con-

tent. The amide carbonyl band spectra of PCYMMA/PMVAc and PCYMMA/PDMA blends show essentially the same features as those of the PCYMMA/PVP blends. The shift is however negligible for PEOx blends. If the frequency shift is

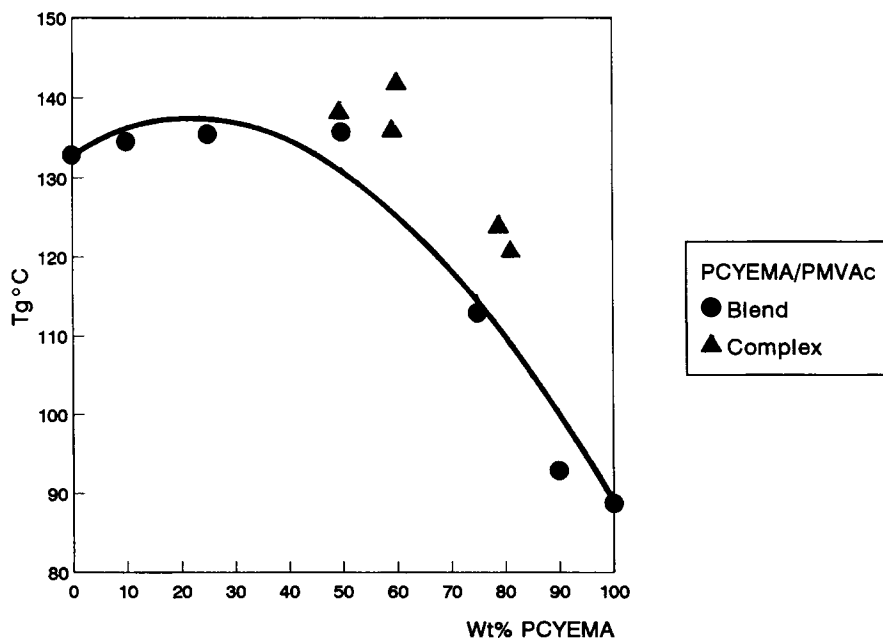


Figure 4 T_g -composition curve of PCYEMA/PMVAc blends ($k = 1.5$, $q = 60$). (●) DMF-cast blend and (▲) complex.

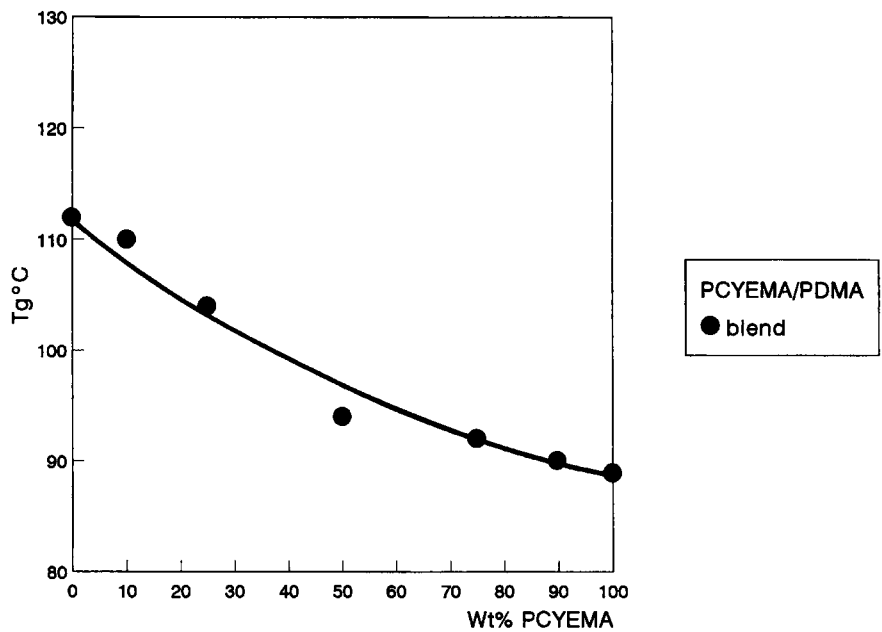


Figure 5 T_g -composition curve of PCYEMA/PDMA blends ($k = 1.0$, $q = -16$).

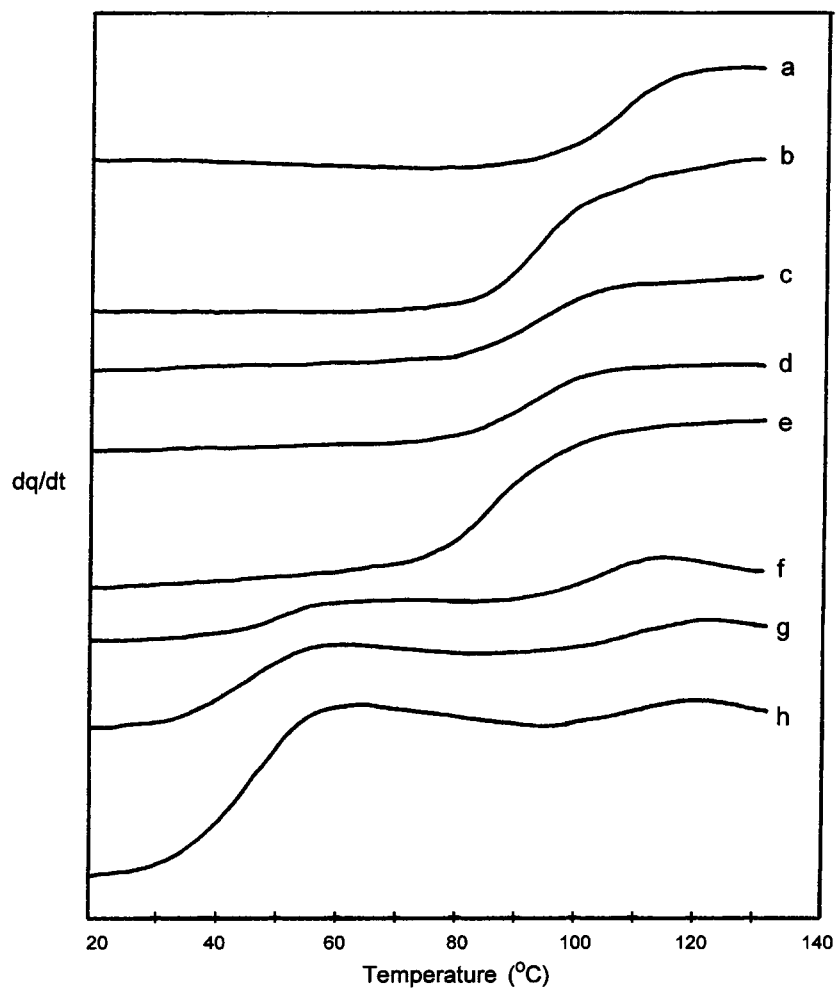


Figure 6 DSC curves of PCYMMA/PEO_x blends: (a) 9 : 1; (b) 7 : 1; (c) 5 : 1; (d) 3 : 1; (e) 2 : 1; (f) 1 : 1; (g) 3 : 1; and (h) 9 : 1.

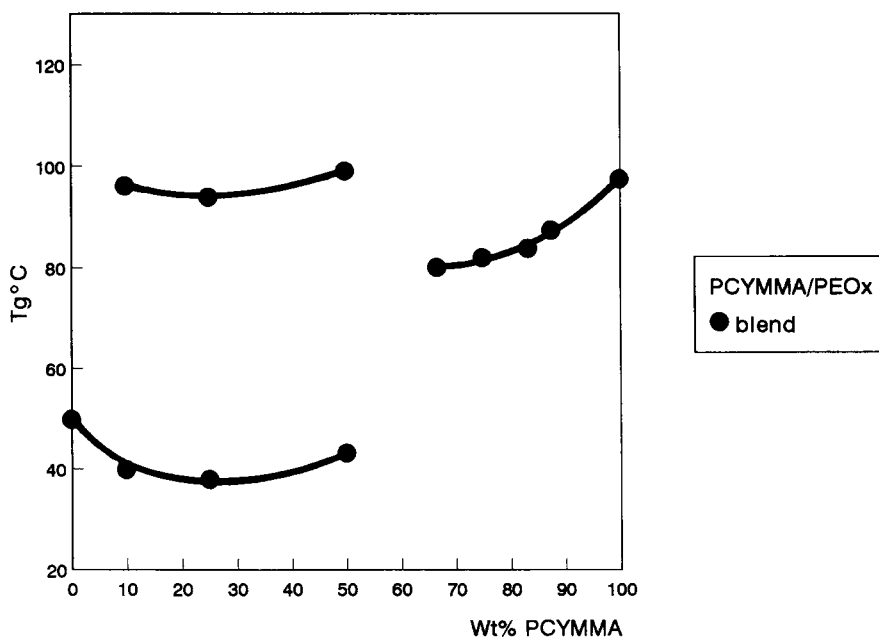


Figure 7 T_g -composition curve of PCYMMA/PEO_x blends.

taken as a measure of polymer-polymer interaction, the intensities of the interaction between PCYMMA and the four tertiary amide polymers are then in the order of PVP ($\Delta\nu = 9 \text{ cm}^{-1}$) > PMVAc ($\Delta\nu = 8 \text{ cm}^{-1}$) > PDMA ($\Delta\nu = 7 \text{ cm}^{-1}$) > PEO_x ($\Delta\nu \approx 0$). The order is in agreement with those observed for blends

of the tertiary amide polymers with hydroxyl-containing polymers.⁷

Figure 10 shows the corresponding FTIR spectra in the amide carbonyl region of PCYEMA/PVP blends. Similar to the PCYMMA blends, the addition of PCYEMA results in the development of sev-

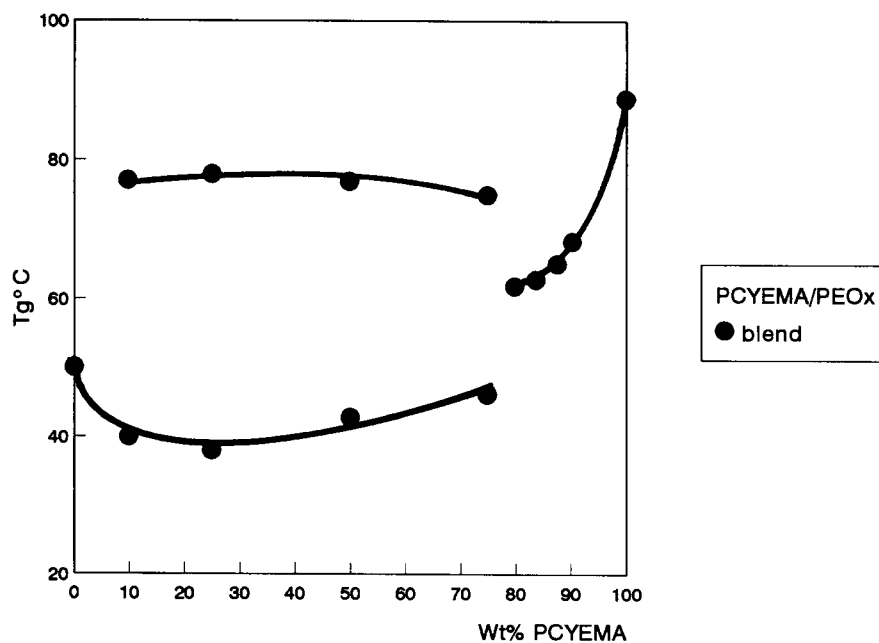


Figure 8 T_g -composition curve of PCYEMA/PEO_x blends.

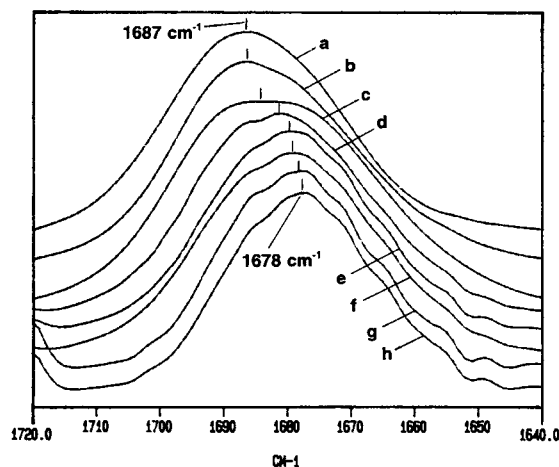


Figure 9 Scale-expanded infrared spectra in the amide carbonyl stretching region of PVP in PCYMMA/PVP blends of varying compositions: (a) pure PVP; (b) 1 : 9; (c) 1 : 5; (d) 1 : 3; (e) 1 : 1; (f) 3 : 1; (g) 5 : 1; and (h) 9 : 1 weight ratio PCYMMA : PVP.

eral overlapping bands. The amide carbonyl band peaks are found once again to shift toward lower frequencies with increasing PCYEMA content. Based on the frequency shifts, the intensities of interaction between PCYEMA and the tertiary amide polymers are in the order of PMVAc ($\Delta\nu = 10 \text{ cm}^{-1}$) > PVP ($\Delta\nu = 8 \text{ cm}^{-1}$) > PDMA ($\Delta\nu = 7 \text{ cm}^{-1}$) > PEOx ($\Delta\nu \approx 1 \text{ cm}^{-1}$). The order differs slightly from that of PCYMMA. It is interesting to note (Fig. 10) the appearance of an additional band at 1635 cm^{-1} for the PCYEMA/PVP blend. The pres-

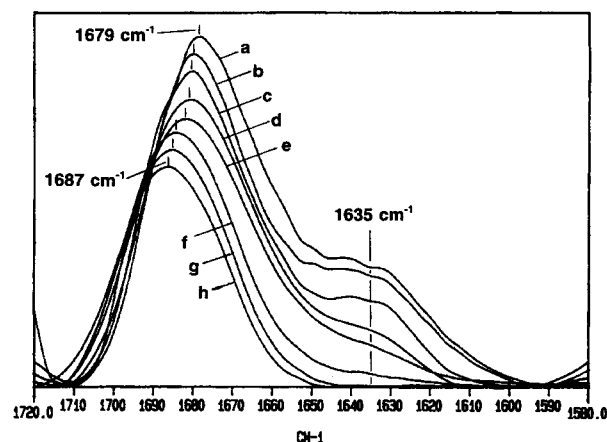


Figure 10 Scale-expanded infrared spectra in the amide carbonyl stretching region of PVP in PCYEMA/PVP blends of varying compositions: (a) 9 : 1; (b) 5 : 1; (c) 3 : 1; (d) 2 : 1; (e) 1 : 1; (f) 1 : 3; (g) 1 : 9 weight ratio PCYEMA : PVP; and (h) pure PVP.

ence of this lower frequency band provides further evidence that the amide carbonyl groups interact with PCYEMA.

In an earlier investigation of miscible blends of PCYEMA with poly(2-hydroxyethyl methacrylate) (PHEMA), we reported that the cyano-absorption band of PCYEMA is shifted to higher frequencies upon mixing with PHEMA.¹⁶ Figure 11 shows the cyano-stretching bands of PCYEMA in the PCYEMA/PVP blends. It is interesting to observe that the cyano-absorption band of PCYEMA at 2253 cm^{-1} has gradually shifted to lower frequencies instead. The observation suggests that the intermolecular interactions between PCYEMA and the tertiary amide polymers are stronger than that between PCYEMA and PHEMA. The extent of the frequency shift depends on the tertiary amide polymer present in the blend and is in the order of PMVAc ($\Delta\nu = 3 \text{ cm}^{-1}$) > PVP ($\Delta\nu = 2 \text{ cm}^{-1}$) > PDMA ($\Delta\nu = 1 \text{ cm}^{-1}$) > PEOx ($\Delta\nu \approx 0$). The shift is negligible for the PEOx blends, showing that PCYEMA interacts poorly with PEOx.

Similar observations of the cyano-absorption band might be expected for the PCYMMA blends. However, the cyano band is not visible in the spectra of all PCYMMA blends. The "quenching" of cyano absorption is known especially for compounds having electronegative atoms, such as oxygen or chlorine, attached to the carbon atom that bears the cyano group.¹⁷

In order to gain further evidence to support the above observations, FTIR studies were also made on liquid mixtures of *N*-methyl-2-pyrrolidone

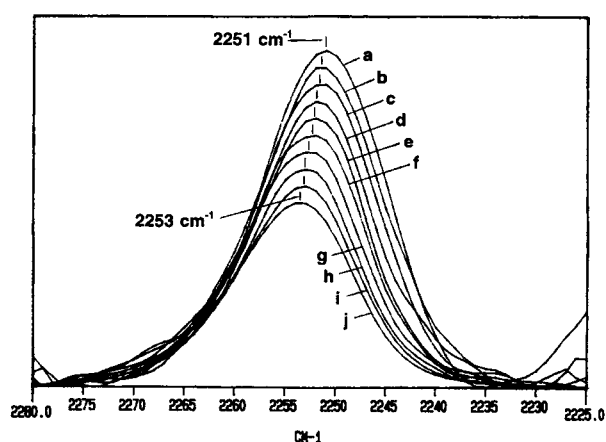


Figure 11 Scale-expanded infrared spectra in the cyano-stretching region of PCYEMA in PCYEMA/PVP blends of varying compositions: (a) 1 : 9; (b) 1 : 5; (c) 1 : 3; (d) 1 : 2; (e) 1 : 1; (f) 2 : 1; (g) 3 : 1; (h) 5 : 1; (i) 9 : 1 weight ratio PCYEMA : PVP; and (j) pure PCYEMA.

(NMP) and benzonitrile. The spectra in the amide carbonyl region and the cyano region are shown in Figures 12 and 13, respectively. The spectra also show similar features as those of the polymer blends. The development of a band at 1635 cm^{-1} is observed in the amide carbonyl region, and the cyano band of benzonitrile at 2228.5 cm^{-1} is shifted to lower frequencies with increasing NMP content.

The above spectroscopic observations suggest that the intermolecular interactions present in the blends may be a form of hydrogen bonding between the carbonyl functional group of the tertiary amide polymers and the methylene hydrogens on the carbon bearing the cyano group in PCYMMA and PCYEMA. Such an interaction could explain the miscibility and the complexation behavior of the various polymer pairs studied.

The distance between the amide carbonyl group and the main polymer chain is a determining steric factor affecting the effectiveness of intermolecular interactions. The closer the amide carbonyl group is to the mainchain, the more difficult it is for intermolecular interaction to establish. Therefore PDMA interacts less effectively with PCYMMA and PCYEMA than PVP or PMVAc does. In the case of PEOx, another steric factor sets in. The nitrogen atom in PEOx is a constituent part of the mainchain and any resonance contribution from this nitrogen will be sterically hindered. Therefore, PEOx is the least effective component polymer in either achieving miscibility or forming complexes.

In summary, PCYMMA forms complexes with PMVAc, PVP, as well as with PDMA; PCYEMA

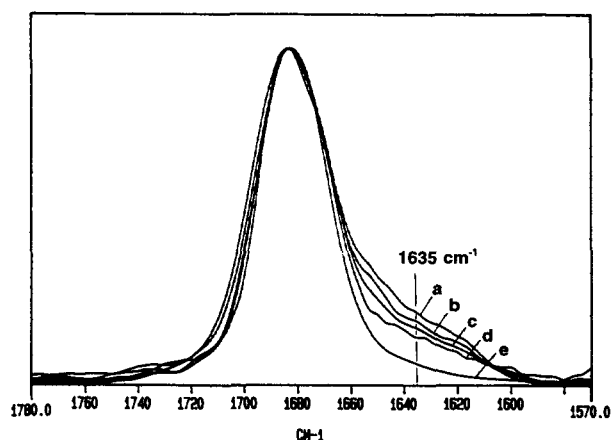


Figure 12 Scale-expanded infrared spectra in the amide carbonyl stretching region of *N*-methyl-2-pyrrolidone (NMP) in NMP/benzonitrile mixtures of varying volume ratios: (a) 1 : 18; (b) 1 : 14; (c) 1 : 12; (d) 1 : 10; and (e) pure NMP.

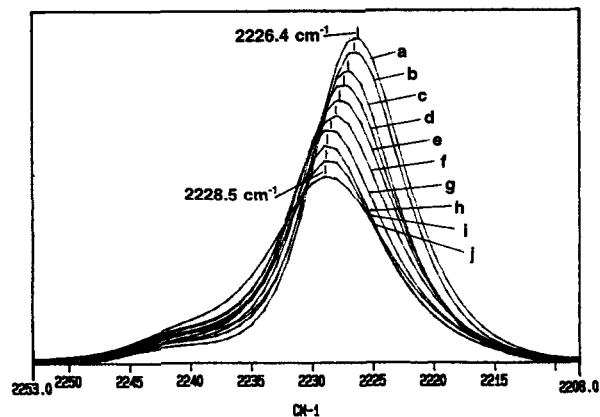


Figure 13 Scale-expanded infrared spectra in the cyano-stretching region of benzonitrile in *N*-methyl-2-pyrrolidone/benzonitrile mixtures of varying volume ratios: (a) 8 : 1; (b) 6 : 1; (c) 4 : 1; (d) 2 : 1; (e) 1 : 1; (f) 1 : 2; (g) 1 : 4; (h) 1 : 6; (i) 1 : 8; and (j) pure benzonitrile.

forms complexes only with PMVAc and PVP. Both cyano-containing PMAs do not form complexes with PEOx. FTIR studies provide evidence on the miscibility behavior through changes in the amide carbonyl absorption band and the cyano-absorption band. Because poly(methyl methacrylate) and poly(ethyl methacrylate) are immiscible with tertiary amide polymers,^{18,19} the present results illustrate the importance of the cyano group in the miscibility and complexation behavior of PCYMMA and PCYEMA.

Financial support of the National University of Singapore is gratefully acknowledged.

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Received May 26, 1994

Accepted September 7, 1994