Novel two-phase polymer system*

Kishore R. Shah†
Hercon Laboratories Corporation, 200B Corporate Court, South Plainfield, NJ 07080, USA

(Received 29 May 1986; accepted 14 October 1986)

Blends of an acrylate or a related copolymer, containing a small proportion of acidic groups, with a homopolymer or a copolymer of an *N*-vinyl lactam were found to exhibit compatibility on an optical scale and a phase-separated microstructure. Infra-red spectroscopic studies of blends of poly(vinyl acetate-*co*-*N*-vinyl 2-pyrrolidone) with poly(2-ethylhexyl acrylate-*co*-acrylic acid) revealed hydrogen bond formation between the pyrrolidone carbonyl groups and the acidic hydrogens. These interpolymer interactions seemed to be the cause of the apparent compatibility of the polymer blends. The existence of microphase separation in the blend was confirmed by transmission electron microscopy. Further manifestation of the two-phase morphology of the blends of this system was obtained in their physical properties, such as stress–strain behaviour of the elastomeric polymer blends and swelling characteristics of the hydrophilic polymer blends.

(Keywords: polymer blends; phase domains; *N*-vinyl lactam; hydrogen bonding; hydrogels)

INTRODUCTION

Studies pertaining to blends of two or more polymers, having different chemical structures and properties, and polymer–polymer interactions have been a field of extensive investigations during the last few years. Polymer blending is an attractive method of preparing new polymeric materials having the desired physical and mechanical properties, on account of the convenience and economics of polymer blending operation as compared to the synthesis of new monomers and polymers. Studies of polymer blends are also of fundamental interest from the viewpoint of thermodynamics of polymer–polymer miscibility. Most physical blends of high molecular weight polymers tend to phase separate, largely due to the fact that only a small gain in entropy occurs upon mixing different kinds of long chains. The phase separation generally results in optical opacity, poor interfacial adhesion and consequently poor mechanical properties. However, a few examples of truly miscible polymer blends are known[1–3].

It is well recognized that, for the attainment of thermodynamic compatibility in a polymer blend, some degree of specific interpolymer interactions leading to a negative enthalpy of mixing is necessary. Thus, for example, strong dispersion forces between phenyl rings of polystyrene and those of poly(2,6-dimethyl-1,4-phenylene oxide) are involved in their blends, for which system Weeks *et al.* have calculated an exothermic heat of mixing[4,5]. It has been suggested that dipole–dipole interactions between the poly(vinylidene fluoride) segments and the carbonyl groups of poly(methyl methacrylate) are sufficiently exothermic to cause miscibility of their blends[6]. Likewise dipolar interactions between the carbonyl groups of polyester and the aromatic rings of polycarbonate are believed to cause their miscibility[7]. Recently Eisenberg and coworkers have reported compatibilization of polystyrene–poly(ethyl acrylate) and polystyrene–polyisoprene blends by incorporation of ionically interacting groups in the corresponding polymeric components[8]. In the case of poly(vinyl chloride)–poly(ε-caprolactone) blends, hydrogen bonding between tertiary hydrogens of the PVC and carbonyl groups of the polyester has been demonstrated[9]. Poly(styrene-*co*-vinylphenyl-hexafluorodimethyl carbinol) has been shown to form miscible blends with bisphenol-A polycarbonate, poly(2,6-dimethyl-1,4-phenylene oxide) and poly(butyl methacrylate) by virtue of interpolymer hydrogen bonding interactions[10]. Cooperative interpolymer hydrogen bonding is also believed to be the driving force in the formation of complex between poly(*N*-vinyl 2-pyrrolidone) and poly(acrylic acid)[11].

One characteristic common to all these blends is their single-phase behaviour, on account of which the blends exhibit physical properties which are an average of those of the corresponding homopolymers. The objective of this paper is to present a new approach to the preparation of blends having a limited but controlled extent of interpolymer hydrogen bonding interactions (*Figure 1*), such that the blends are compatible on an optical scale, but they exhibit microphase separation. Such blends are characterized by their unique physical properties arising from their two-phase morphology. An important feature of these blends is that one of the two components is either a homopolymer or a copolymer of an *N*-vinyl lactam, and the other component is an acrylate or a related copolymer containing a small proportion of acidic groups. Several applications of this system for the development of new polymeric materials have been reported elsewhere[12–17].

EXPERIMENTAL

Materials

Poly(*N*-vinyl 2-pyrrolidone) (K-90 grade) was obtained from GAF Corporation. The various copolymers were prepared by conventional free-radical initiated

---

* Presented at the Americal Chemical Society Meeting, Miami Beach, Florida, USA, April 1985.

† Formerly of The Kendall Company, 17 Hartwell Avenue, Lexington, MA, USA, where the work was done.

0032–3861/87/071212–05$03.00

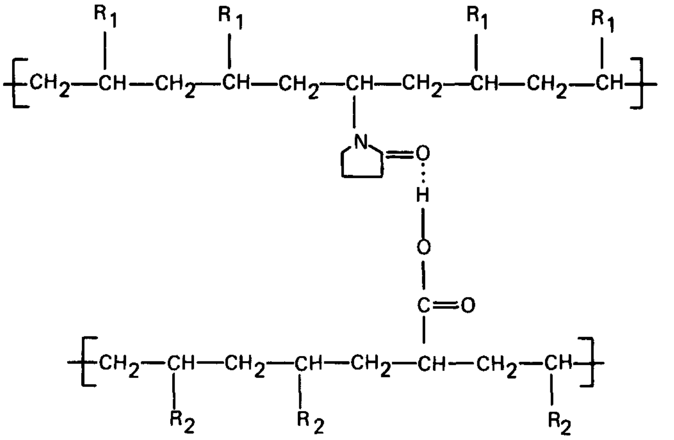

Figure 1 Interpolymer hydrogen bond formation

solution polymerization, the details of which are described elsewhere[12-14].

The blends were prepared by dissolving together the weighed amounts of the respective polymeric components in a mutual solvent such as chloroform, *N*,*N*-dimethylformamide, or 2-methoxyethanol, and then isolating the blend by evaporation of the solvent under vacuum at 60–80°C.

Methods

A Perkin–Elmer 283 i.r. spectrophotometer was used for infra-red measurements. Spectra of the blends and copolymers in the dry state were obtained on films cast from chloroform solution on KBr plates. The solution spectra were obtained utilizing 0.035 mm matched KBr cells.

Transmission electron micrographs were taken employing a Philips 300 electron microscope. Specimens of 0.2 × 0.2 mm cross section and lengths ranging from 2 to 10 mm were exposed to osmium tetroxide vapour at room temperature for one week in order to stain the pyrrolidone groups selectively. After this treatment, the specimens turned black, indicating effective staining. Portions of the stained specimens were embedded in epoxy resin, trimmed to a truncated pyramid shape, and ultramicrotomed using a diamond knife to a thickness of 600–800 Å before taking the micrographs.

The stress–strain data on the elastomeric materials were obtained using ASTM procedure D-412 on an Instron model 1122 testing instrument. The test samples were die cut from 2–3 mm thick sheets, which were prepared by compression moulding in a press at 170°C. Measurements for all the compositions were made in triplicate.

Samples of the hydrophilic blends for swelling measurements were prepared by compression moulding 0.2 to 0.3 mm thick films of the blend at 190°C. The films were then equilibrated in distilled water at 22°C for 3 days, frequently changing the water during this period, to form hydrogels. The water content of the hydrogels was determined by the difference in weights of the blend samples before and after hydration:

$$\text{water content of hydrogel}\ (\%) = \frac{\text{wt of hydrogel} - \text{wt of dry blend}}{\text{wt of hydrogel}} \times 100$$

Surface water of the hydrated samples was removed prior to weighing by blotting between filter papers. Measurements were made in triplicate for each of the blend compositions.

RESULTS AND DISCUSSION

Polymer blend compatibility

Blends of each of the *N*-vinyl lactam homopolymers and copolymers (*Table 1*) with each of the copolymers (*Table 2*), containing small amounts of acidic groups, were found to be optically transparent. This apparent compatibility extended over the entire range of blend ratios. However, blends of an *N*-vinyl lactam homopolymer, such as poly(*N*-vinyl 2-pyrrolidone) (PVP), with an acrylic polymer, such as poly(ethyl acrylate) or poly(methyl methacrylate), which does not have acidic groups, are known to exhibit macroscale phase separation indicated by their optical opacity. Interactions between the acidic groups and the lactam groups of the respective polymeric components, therefore, must be responsible for the observed compatibility of the blends of this system.

Infra-red spectroscopic studies (*Figures 2–4*) of blends of poly(vinyl acetate-*co*-*N*-vinyl 2-pyrrolidone) (VA/VP copolymer, 36% VP) with poly(2-ethylhexyl acrylate-*co*-acrylic acid) (EHA/AA copolymer, 8% AA) have indeed revealed the existence of hydrogen bonds between the pyrrolidone carbonyl and carboxyl groups. *Figure 2* shows the infra-red spectra of the VA/VP copolymer, the EHA/AA copolymer, and their blend containing 1:1 molar equivalence of the pyrrolidone and the carboxyl groups. The pyrrolidone carbonyl absorption of the VA/VP copolymer was observed at 1680 cm^{-1}, at which frequency the EHA/AA copolymer showed a negligible absorption. The spectrum of the blend of the two copolymers showed two absorptions (1680 and 1640 cm^{-1}) due to the pyrrolidone carbonyl group. The 1640 cm^{-1} peak may be ascribed to the hydrogen-bonded

Table 1 *N*-Vinyl lactam polymers and copolymers

Poly( )	Comonomer ratio (wt %)
N-Vinyl 2-pyrrolidone (VP)	
N-Vinyl caprolactam	
Vinyl acetate-*co*-VP	70:30
Vinyl acetate-*co*-VP	45:55
Methyl methacrylate-*co*-VP	75:25
n-Butyl methacrylate-*co*-VP	80:20
N,*N*-Dimethylacrylamide-*co*-VP	68:32
N,*N*-Dimethylacrylamide-*co*-vinyl acetate-*co*-VP	50:22:28

Table 2 Acidic-group-containing copolymers

Poly( )	Comonomer ratio (wt %)
2-Ethylhexyl acrylate-*co*-acrylic acid	96:4
n-Butyl acrylate-*co*-acrylic acid	96:4
Ethyl acrylate-*co*-acrylic acid	96:4
Methyl methacrylate-*co*-methacrylamide-*co*-acrylic acid	65:30:5
n-Butyl methacrylate-*co*-methacrylamide-*co*-acrylic acid	80:15:5
2-Ethylhexyl acrylate-*co*-methacrylamide-*co*-acrylic acid	65:30:5
Styrene-*co*-methacrylamide-*co*-acrylic acid	65:30:5
Methyl methacrylate-*co*-2-acrylamido-2-methylpropanesulphonic acid	90:10
n-Butyl methacrylate-*co*-2-hydroxyethyl methacrylate-*co*-acrylic acid	52:40:8
n-Butyl methacrylate-*co*-*p*-styrenesulphonamide-*co*-acrylic acid	62:30:8

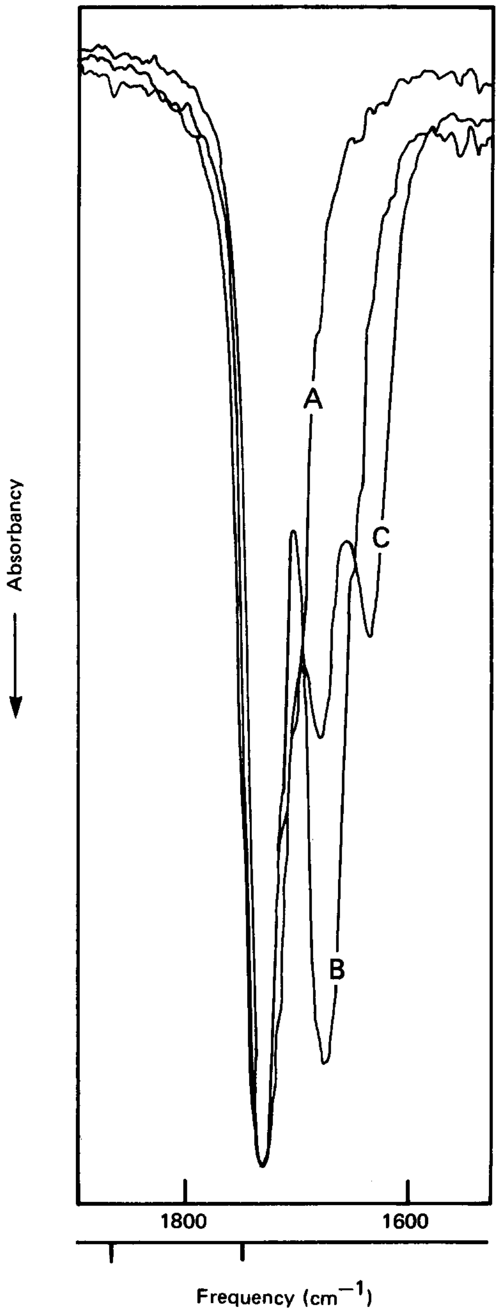

Figure 2 I.r. spectra of the EHA/AA copolymer (A), the VA/VP copolymer (B) and the EHA/AA–VA/VP copolymer blend (C)

pyrrolidone carbonyl group[11]. *Figures 3* and *4* illustrate the effect of the nature of solvent on the pyrrolidone carbonyl absorption in solutions of a blend of the two copolymers having a slight excess of carboxyl groups. The 1640 cm^{-1} peak due to the hydrogen-bonded carbonyl group was absent in the spectrum (*Figure 3*) of a 10% solution of the blend of the two copolymers in chloroform, which has an acidic hydrogen capable of interfering or competing with the pyrrolidone carbonyl and the carboxyl group interactions. In contrast, the spectrum (*Figure 4*) of the same blend in benzene showed a strong hydrogen-bonded pyrrolidone carbonyl absorption.

Transmission electron microscopy of these blends has further indicated that, although the blends were optically clear, they exhibited microphase separation. Thus, for example, an electron micrograph (*Figure 5*) of a blend of the VA/VP and the EHA/AA copolymers at 2:3 weight ratios showed the VA/VP copolymer, which was selectively stained with osmium tetroxide, as the dispersed phase, the domains of which ranged from 200 to 1000 Å in size.

One may reasonably expect such microphase separation to be a general characteristic of this system of polymer blends. Further, the extent of hydrogen bonding interactions is likely to influence the morphology of the blend. The greater the extent of these interactions, the smaller would be the expected domain size of the dispersed polymeric phase. The two-phase microstructure of these blends differentiates them from the complexes formed between PVP and polyacids, such as poly(acrylic acid) (PAA). Dynamic mechanical properties of films of the PVP–PAA complex have indicated that the two polymeric components were homogeneously distributed throughout the films[18].

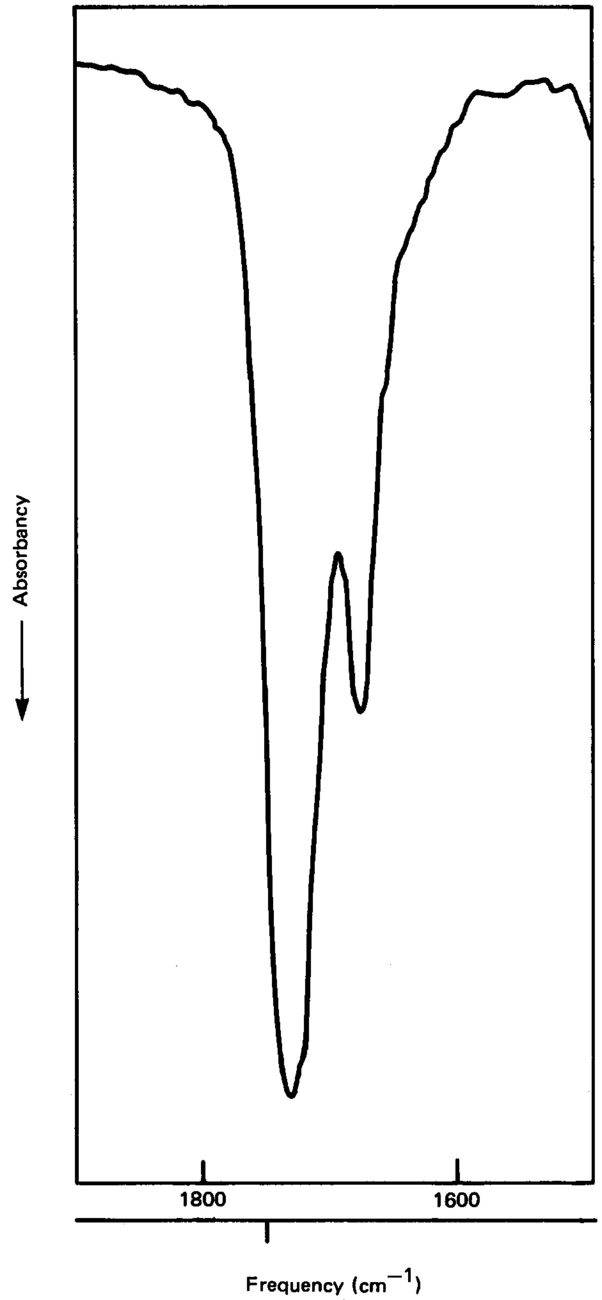

Figure 3 I.r. spectrum of the EHA/AA–VA/VP copolymer blend in chloroform

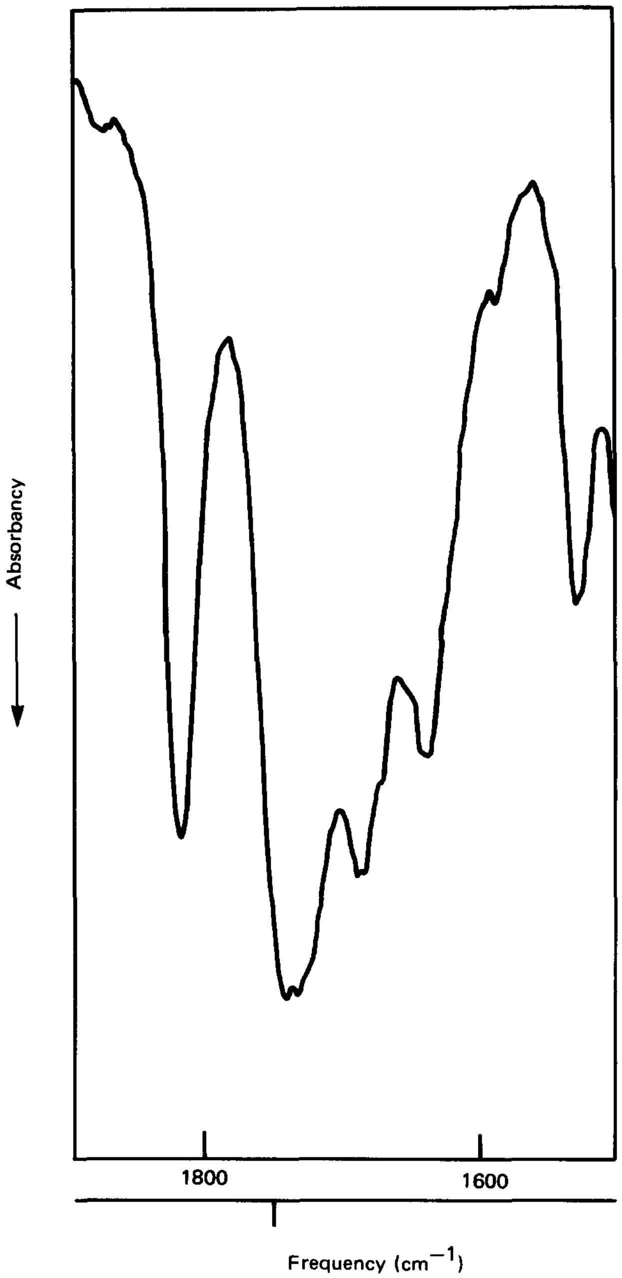

Figure 4 I.r. spectrum of the EHA/AA–VA/VP copolymer blend in benzene

Further manifestation of the two-phase morphology of blends of this system was obtained in their physical and mechanical properties, such as stress–strain behaviour of the elastomeric acrylic polymer blends and swelling characteristics of the hydrophilic polymer blends.

Elastomeric acrylic polymer blends

The polymer blends, in which a rubbery poly(ethyl acrylate-*co*-acrylic acid) was the major component and a glassy homopolymer or a copolymer of *N*-vinyl 2-pyrrolidone was the minor component, exhibited thermoplastic elastomeric characteristics[13]. The effect of blending an ethyl acrylate copolymer containing 4% acrylic acid (EA/AA copolymer) with a glassy polymer can be seen from the stress–strain measurements of the blends (*Table 3*). The EA/AA copolymer by itself was rubbery; but being uncrosslinked, it had poor strength. The glassy polymer had strength but not elasticity. On the other hand, the blends exhibited both high elongation and enhanced tensile strength. These properties of the blends may be interpreted in terms of the reinforcement of the rubbery EA/AA copolymer matrix with the domains of the glassy copolymer, which serve as points of thermally reversible pseudocrosslinks. A useful feature of the blends was the absence of covalent crosslinkages, on account of which they were processable by thermoplastic methods.

Water-swellable polymer blends

It was of obvious interest to study the compatibility of the hydrophobic/hydrophilic polymer blends in an aqueous environment. Although the blends, containing hydrophilic polymer (e.g. PVP) as the major component, were coherent and optically transparent in the dry state, most of them became opaque and incoherent when placed in water. A few blends even disintegrated into crumbs by the effect of hydration. However, blends of PVP (and those of water-soluble *N*-vinyl lactam copolymers) with acidic-group-containing water-insoluble copolymers, having a certain hydrophobic–hydrophilic balance, retained coherency and optical transparency upon equilibration in water to form unusually strong and stable hydrogels[12]. In addition, because of the absence of covalent crosslinks, the hydrogel-forming blends were amenable to thermoplastic methods of processing such as solution casting and moulding.

The equilibrium water content of some of the polymer blend hydrogels is summarized in *Table 4*. The equilibrium hydration of blends of poly(n-butyl methacrylate-*co*-methacrylamide-*co*-acrylic acid) (terpolymer) with PVP and with poly (*N*,*N*-dimethylacrylamide-*co*-*N*-vinyl 2-pyrrolidone) (DMA/VP copolymer) was found to vary inversely with the proportion of the terpolymer in the blend (*Figure 6*). This swelling behaviour is analogous to that of the covalently crosslinked hydrogels, in which their water content is inversely proportional to the amount of crosslinking agent present in the polymerization mixture[19]. Thus, the possible domains of the water-insoluble terpolymer in the blend seemed to function as pseudocrosslinks to insolubilize the water-soluble component in the blend. The hydrogels were stable in the aqueous medium over a pH range of 1 to 11 and in dilute salt solutions (e.g. normal saline). This stability of the polymer blend network implies that interpolymer

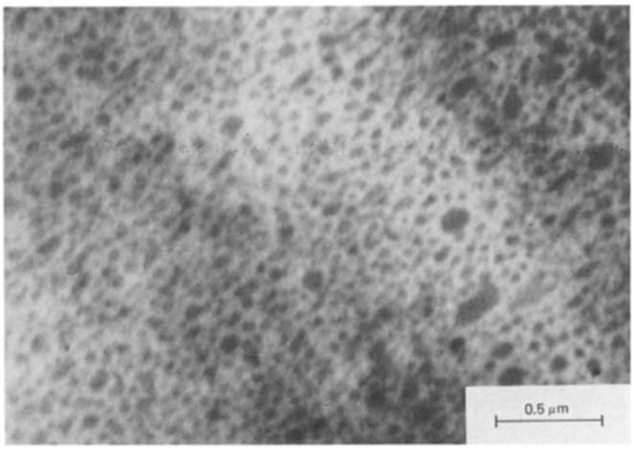

Figure 5 Transmission electron micrograph of the EHA/AA–VA/VP copolymer blend

Table 3 Stress–strain properties of blends of the EA/AA copolymer with glassy polymers

Glassy polymer composition[a] (wt%)				Glassy polymer in blend (wt%)	Tensile strength (MPa) at			Elongation at break (%)
BMA	VA	MMA	VP		100%	300%	Break	
				0	0.276	0.490	0.731	1285
			100	10	0.621	1.379	4.861	738
80			20	20	0.993	2.186	3.378	570
	70		30	20	0.627	1.351	3.213	617
	45		55	20	2.379	5.171	7.302	426
		75	25	20	1.165	3.096	5.964	485

[a] BMA, n-butyl methacrylate; VA, vinyl acetate; MMA, methyl methacrylate; VP, *N*-vinyl 2-pyrrolidone

Table 4 Water content of PVP–blend hydrogels

Blend composition		Equilibrium water content (wt%)
Water-insoluble copolymer[a] (wt%)	PVP (wt%) in blend	
MMA–MAA–AA (65:30:5)	70 90	68 91
Styrene–MAA–AA (65:30:5)	70 90	58 80
BMA–HEMA–AA (52:40:8)	70 90	76 89
MMA–AMPS (90:10)	90	84

[a] MMA, methyl methacrylate; MMA, methacrylamide; AA, acrylic acid; BMA, n-butyl methacrylate; HEMA, 2-hydroxyethyl methacrylate; AMPS, 2-acrylamido-2-methylpropanesulphonic acid

hydrogen bonding alone cannot be the force preventing the dissolution of the water-soluble polymeric component in water, because water would be expected to disrupt the hydrogen bonds under the above experimental conditions. A hypothesis for this observed stability may be that the two polymeric phases were not pure, and that the segments of the water-soluble polymer were trapped in the domains of the water-insoluble polymer.

CONCLUSIONS

Blends of an acrylate or a related copolymer, containing a small proportion of acidic groups, with a homopolymer or a copolymer of an *N*-vinyl lactam exhibit compatibility on an optical scale and a phase-separated microstructure. Interpolymer hydrogen bonding interactions between the lactam carbonyl groups and the acidic hydrogens seem to be the cause of this apparent compatibilization. Properties of the blends can be tailored over a wide range by judicious selection of the chemical composition of the individual polymeric components and the extent of interpolymer hydrogen bonding.

ACKNOWLEDGEMENTS

The author is grateful to The Kendall Company for releasing this paper for publication. The author also thanks Dr David Thomas, Lehigh University, Bethlehem, PA, for the electron micrograph.

REFERENCES

1 Cizek, E. P. US Patent 3383435 (14 May 1968)
2 Koleske, J. V. and Lundberg, R. D. *J. Polym. Sci.* (*A*-2) 1969, **7**, 795
3 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility', Academic Press, New York, 1979, Ch. 5

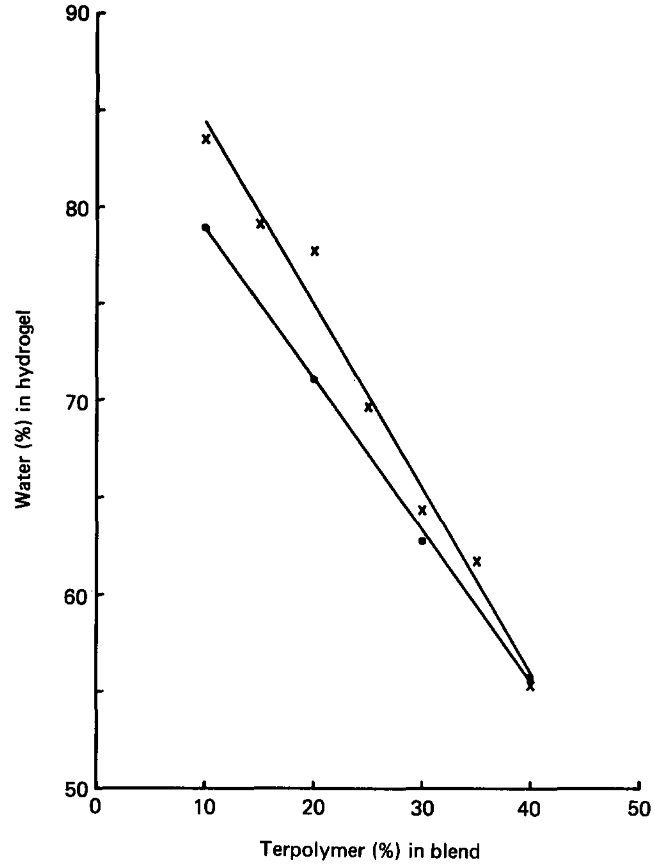

Figure 6 Equilibrium hydration of the PVP–terpolymer (×) and the DMA/VP copolymer–terpolymer (○) blends (terpolymer = 73% BMA, 22% MAA and 5% AA; DMA/VP copolymer = 68% DMA and 32% VP)

4 Wellinghoff, S. T., Koenig, J. L. and Baer, E. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 1913
5 Weeks, N. E., Karasz, F. E. and MacKnight, W. J. *J. Appl. Phys.* 1977, **48**, 4068
6 Paul, D. R., Barlow, J. W., Bernstein, R. E. and Wahrmund, D. C. *Polym. Eng. Sci.* 1978, **18**, 1225
7 Cruz, C. A., Barlow, J. W. and Paul, D. R. *Macromolecules* 1979, **12**, 726
8 Eisenberg, A., Smith, P. and Zhou, Z.-L. *Polym. Eng. Sci.* 1982, **22**, 1118
9 Olabisi, O. *Macromolecules* 1975, **9**, 316
10 Pearce, E. M., Ting, S. P. and Kwei, T. K. *J. Polym. Sci., Polym. Lett. Edn.* 1980, **18**, 201
11 Boyer-Kawenoki, F. *C.R. Acad. Sci. Paris C* 1966, **263**, 278
12 Shah, K. R. US Patent 4300820 (17 Nov. 1981)
13 Shah, K. R. and Temin, S. C. US Patent 4306039 (15 Dec. 1981)
14 Shah, K. R. US Patent 4337325 (29 Jun. 1982)
15 Shah, K. R. US Patent 4369229 (18 Jan. 1983)
16 Shah, K. R. US Patent 4370380 (25 Jan. 1983)
17 Shah, K. R. US Patent 4462665 (31 Jul. 1984)
18 Tsutsui, T., Nakano, H., Tanaka, R. and Tanaka, T. *Kobunshi Ronbunshu* 1978, **35**, 517; *Chem. Abstr.* 1978, **89**, 147505
19 Refojo, M. F. *J. Appl. Polym. Sci.* 1965, **9**, 3161