

Copolymerizations involving *N*-vinyl-2-pyrrolidone

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Low conversion copolymerizations have been conducted with *N*-vinyl-pyrrolidone (VP) as monomer-1 and the following reagents were used as monomer-2: acryloxymethylpentamethyldisiloxane (AMS), methacryloxymethylpentamethyl disiloxane (MMS), *n*-butyl acrylate (BA) and 2-hydroxyethylmethacrylate (HEMA). In the same order the derived monomer reactivity ratios (r_1, r_2) were (0.34, 1.57); (0.04, 4.92); (0.02, 0.80) and (0.05, 3.12). For a range of different feed compositions within each system integral curves were thereby computed for the instantaneous copolymer composition throughout all stages of conversion. These gave predictions on compositional heterogeneity which compared satisfactorily with the clear, translucent or opaque appearance of copolymers prepared to very high conversion via γ -irradiation. However, the VP-HEMA system, for which there is no azeotropic composition, yielded optically clear copolymers at all feed compositions. This finding is explained on the basis of the almost iso-refractive nature of the two homopolymers and/or strong thermodynamic compatibility among copolymers and homopolymers as evidenced by a single T_g observed on cast films.

(Keywords: poly(*N*-vinyl-2-pyrrolidone); poly(2-hydroxyethyl methacrylate); reactivity ratio; compositional heterogeneity; glass transition temperature; refractive index)

INTRODUCTION

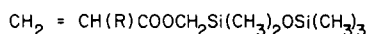
In addition to the abbreviations already indicated in the abstract, the following are also adopted:

AZPA = 4,4'-azobis-4-cyanopentanoic acid

DMF = dimethyl formamide

PTFE = polytetrafluoroethylene

The following denotes the formulae of AMS (with R = H) and MMS (with R = CH₃).



Although poly-HEMA itself is not soluble in water, the considerable swelling in water of polymerized or copolymerized HEMA is sufficient to yield several useful hydrogels. The monomer reactivity ratios of HEMA with other monomers have been reported by us previously¹. VP [systematic name 1-(2-oxo-1-pyrrolidinyl)ethylene] is another monomer used frequently in the preparation of hydrogels. Poly-VP is rather unusual in the respect that it is soluble not only in water but also in some organic solvents. The physico-chemical principles underlying the application of poly-VP have been reviewed by Molyneux². Rothschild has demonstrated³ that binding of water and other hydrogen donors takes place not only at the carbonyl group of the lactam but also involves the C-N bond.

The authors are currently engaged in a programme on the preparation and characterization of hydrogels based on copolymers of VP. Relatively few reactivity ratios have been reported for copolymerizations involving VP. The determination of reactivity ratios for the copolymeri-

zation of VP with potentially useful co-monomers forms the main basis for the present communication. Some observations are also made on predicted and experimental effects at high conversion.

EXPERIMENTAL

Materials

VP (Aldrich Chem. Co.) was dried over anhydrous MgSO₄ and vacuum distilled in the presence of hydroquinone (b.p. 68°C at 2 mm Hg). AMS and MMS were prepared and purified as described previously¹. The AMS was subjected to further purification by column chromatography using silica gel as absorbent and *n*-hexane/diethylether (3:1 v/v) as eluant. Poly-HEMA was prepared in the absence of any crosslinking agent according to the procedure described earlier⁴. The intrinsic viscosity in DMF at 25°C in conjunction with literature values⁵ for the Mark-Houwink constants gave a molar mass of $6.02 \times 10^5 \text{ g mol}^{-1}$. Poly-VP samples of nominal molar mass $4.0 \times 10^4 \text{ g mol}^{-1}$ and $7.0 \times 10^5 \text{ g mol}^{-1}$ were obtained from Phase Separation Ltd. and B.D.H. respectively.

Reactivity ratio determination

As indicated in Table 1 copolymerization was effected either in outgassed, sealed ampoules or in PTFE centrifuge tubes ('Nalgene'—obtained from Baird Tatlock) under nitrogen, the tubes being fitted with PTFE screw caps. The initial mole fraction (f_1) of monomer-1 was varied over at least a ten-fold range. The conversions were generally below 10%, but the time to attain such conversion for any system varied with f_1 . Hence in Table 1 only an approximate order of such time is indicated.

Table 1 Reaction conditions for low conversion copolymerization used for determination of reactivity ratios

Monomer-2	Reaction vessel	Medium	Temp. (°C)	Initiator concentration (mol l ⁻¹)	Solvent	Monomer/solvent ratio (v/v)	Number of feed compositions	Range of f_1	Approx. time for 10% conversion (h)
AMS	PTFE tubes	N ₂	65	AZPA, 1 × 10 ⁻³	Ethanol	1:1	9	0.03–0.38	3 $\frac{3}{4}$
BA	PTFE tubes	N ₂	70	AZPA, 1 × 10 ⁻³	Cyclohexanone	1:1	9	0.075–0.86	$\frac{1}{2}$
HEMA	PTFE tubes	N ₂	65	AZPA, 1 × 10 ⁻³	Ethanol	1:1	12	0.09–0.76	2
MMS	Glass ampoules	Vacuum	65	AZPA, 1 × 10 ⁻⁷	In bulk	∞	10	0.02–0.89	$\frac{1}{2}$

For the system involving BA and HEMA, petroleum ether (b.p. 40°–60°C) was used as precipitant. For the VP/MMS system the reaction medium was diluted with an equal volume of ethanol and precipitated in water. VP/AMS copolymers of high VP content could be precipitated in petroleum ether (b.p. 40°–60°C). Those of lower VP content did not precipitate and could only be isolated by precipitation in water. All copolymers were washed with petroleum ether (b.p. 40°–60°C) and dried *in vacuo* at 40°C.

Analysis of copolymer

For all systems, the VP content was determined by analysis for nitrogen using a Tecator Kjeltach Auto Analyser on approximately 0.06–0.10 g samples at maximum operation temperature. A Tecator 1007 digester was used for the initial digestion of the samples. A poly-VP sample was analysed within each set of copolymers to assess the accuracy of the method. The theoretical percentage of nitrogen in poly-VP is 12.6. A correction factor, $G = (12.6)/(\text{experimental percentage nitrogen for poly-VP})$ was used. Generally, the value of G was approximately 1.02–1.05. A slight modification to the normal manufacturer's procedures was made to allow for the vigorous reaction that occurred in the initial stages of digestion, viz. the T1007 digester was not allowed to heat up prior to digestion, but was only switched on when the samples were in place.

For VP/HEMA copolymers, the analysis was also made by analysing for the hydroxyl group content using samples of about 0.1 g, the procedure being as indicated previously¹.

Copolymerization to high conversion

For each monomer pair, mixtures affording 8 different values of f_1 were introduced into previously siliconized borosilicate glass ampoules. The ampoules were out-gassed by freeze–thaw cycles at 10⁻⁵ mm Hg and sealed. Irradiation was effected at 21°C with γ -irradiation from a 9000 Ci⁶⁰Co source to a total dose of 1 Mrad. The dose rate determined by Fricke dosimetry was 0.01 Mrad h⁻¹.

Casting films of polymer mixtures

A mutual solvent for poly-VP, poly-HEMA and VP/HEMA copolymer is ethanol, which was used to prepare the relevant solutions. Films were cast on microscope slides by slow evaporation of solvent at room temperature (~20°C). For solutions containing poly-HEMA or poly-HEMA in admixture with another component, disso-

lution was enhanced by the addition of a small quantity of water.

Initial qualitative tests were made with different mixtures of poly-HEMA and poly-VP, the content of the latter varying for 10% to 90% of the total homopolymer mixture. Solutions of poly-HEMA in ethanol and poly-VP in ethanol were made up separately and these were mixed in varying proportions. The slight turbidity which resulted on mixing could be dispelled on addition of a trace of water⁴. However, if too much water was added, the resultant films were opaque. Subsequently the following films were made:

- poly-HEMA
- a VP-HEMA copolymer comprising 25 wt% VP
- a copolymer/homopolymer mixture containing 25 wt% VP. This was made by mixing poly-VP with a copolymer of composition 4 wt% VP
- a copolymer/homopolymer mixture containing 25 wt% VP. This was made by mixing poly-HEMA with a copolymer of composition 34 wt% VP
- a mixture of poly-VP with poly-HEMA in which the content of poly-VP was 25 wt%
- poly-VP.

All the above films were cast from 1% w/v solutions made up by dissolving the weighed component or mixed components directly in ethanol.

Systems containing poly-HEMA (a, d and e) required 1–2 drops of water per 10 cm³ solution in order to enhance dissolution. All the solutions were clear.

Glass transition temperature (T_g)

Dry cast films were scraped from microscope slides and ground into a powder. The T_g of each sample (10–20 mg) was measured in air with a Perkin Elmer Differential Scanning Calorimeter (Model DSC-2). The heating rate was 20°C min⁻¹ and the temperature range covered was 50°–200°C.

Refractive indices

A 10% (w/v) solution of polymer in ethanol was used to cast a film directly on the prism of an Abbé refractometer, which was fitted with an external recirculating thermostat. The solution was covered by an inverted watch glass and allowed to dry slowly at room temperature to leave a film. Any minute traces of residual solvent were removed by raising the temperature to 40°C before taking refractive index readings (n_D) at 20°C for both poly-HEMA and poly-VP.

RESULTS

Reactivity ratios

The Mayo-Lewis⁶, Fineman-Ross⁷ and Kelen-Tüdös graphical procedures were used to determine the reactivity ratios r_1 and r_2 for the VP/monomer-2 systems. The plots are not reproduced here and reference should be made to the original papers for details of the relevant coordinates. The results are given in Table 2. For the VP/BA system the Mayo-Lewis intersection method afforded an r_2 value of similar magnitude to that yielded by the other two procedures. However, the value of r_1 was extremely large and this has been excluded from the Table. The quoted overall uncertainties in the average values of r_1 and r_2 do not follow obviously from inspection of the r_1, r_2 values listed. This is because they are based on *unquoted individual uncertainties* for each *separate* procedure. It is to be noted that the uncertainties quoted in the Table would become considerably reduced, if results via the Mayo-Lewis procedure were excluded from consideration.

High conversion copolymerization

After γ -irradiation the copolymers were removed from their ampoules in the form of solid rods. Following oven curing for 24 h at 100°C the percentage conversions were found to be 86–92, 99.9, 98 and 85–90 for copolymerizations involving AMS, BA, HEMA and MMS respectively. The mole fractions of VP in the feed (f_1) are thus close to those in the copolymer (F_1). The rods were assessed visually for optical homogeneity as clear (c), clear-translucent (c/t), translucent (t), translucent-opaque (t/o) or opaque (o). The observations have been reported already⁹ for the system VP/BA, but are included here also to afford comparison with the other systems.

VP/AMS:

$f_1 = 0.220, 0.325, 0.472, 0.594$ and 0.693 --all (t).
 $f_1 = 0.894$ (t/o)
 $f_1 = 0.957$ (o)

VP/BA:

$f_1 = 0.112, 0.223, 0.331, 0.435, 0.535$ and 0.584 --all (c)
 $f_1 = 0.633$ (c/t)
 $f_1 = 0.681, 0.728$ (t)
 $f_1 = 0.775$ (t/o)
 $f_1 = 0.821, 0.867, 0.912$ (t)
 $f_1 = 0.956$ (o)

VP/HEMA:

$f_1 = 0.145, 0.239, 0.333, 0.473, 0.631, 0.707$ --all (c)

VP/MMS:

$f_1 = 0.043, 0.104, 0.198, 0.357, 0.487, 0.596, 0.689$ --all (c/t)
 $f_1 = 0.769, 0.838, 0.899, 0.952$ --all (t)
 $f_1 = 0.977$ (o)

These observations may be compared with the compositional drift of copolymer with increasing fractional conversion (C) predicted from the Skeist equation¹⁰

$$\ln(1-C) = \int_{f_{1i}}^{f_{1j}} \frac{df_1}{(F_1 - f_1)} \quad (1)$$

Here one calculates C when f_1 changes during this conversion from a value f_{1i} to a value f_{1j} . We have found it convenient to use equation (2) due to Meyer and Lowry¹¹, this expression being an integral form of equation (1)

$$C = \left(\frac{f_{1j}}{f_{1i}}\right)^\alpha \left(\frac{1-f_{1j}}{1-f_{1i}}\right)^\beta \left(\frac{f_{1i}-\delta}{f_{1j}-\delta}\right)^\gamma \quad (2)$$

In equation (2) $\alpha = r_2/(1-r_2)$; $\beta = r_1/(1-r_1)$; $\gamma = (1-r_1r_2)/[(1-r_1)(1-r_2)]$; $\delta = (1-r_2)/(2-r_1-r_2)$.

The computations were made by means of a program developed here. It was written in Fortran 77 for use on the Prime 750 and the diagrams were produced on a Calcomp 1051 plotter. The resultant curves of C versus instantaneous copolymer composition (F_1) for copolymerizations involving VP with AMS, BA, HEMA and MMS are shown in Figures 1–4 respectively. In each instance the initial feed compositions (f_1) were selected from among the actual values used in the γ -initiated, high conversion experiments. An azeotropic composition is not possible for the systems in Figures 1, 3 and 4, since the condition that r_1 and r_2 should both be >1 or both <1 is not fulfilled. For VP/BA (Figure 2) the azeotropic composition (f_1)_c is given by

$$(f_1)_c = (1-r_2)/(2-r_1-r_2) = 0.165 \quad (3)$$

The curve corresponding to (f_1)_c is included in Figure 2 as curve a.

Compatibility in VP/HEMA system

As noted, there is considerable compositional heterogeneity in VP/HEMA copolymers throughout the conversion. However, over a wide range of f_1 the copolymers produced to high conversion remain optically clear. One possible reason for this is considered to lie in the refractive indices of the polymers. Attention is focused solely on a temperature of 20°C, which is the temperature at which the copolymers are formed and also that at which films of mixture were cast for T_g determination (see later).

Table 2 Monomer reactivity ratios for the copolymerizations of VP with AMS, BA, HEMA and MMS

Procedure	VP(1)/AMS(2)		VP(1)/BA(2)		VP(1)/HEMA(2)		VP(1)/MMS(2)	
	r_1	r_2	r_1	r_2	r_1	r_2	r_1	r_2
Mayo-Lewis	0.34	1.60	–	0.80	0.02	2.98	0.05	4.95
Fineman-Ross	0.33	1.52	0.02	0.78	0.09	3.40	0.05	4.98
Kelen-Tüdös	0.34	1.58	0.02	0.82	0.03	2.97	0.01	4.83
Average values	0.34 ± 0.05	1.57 ± 0.18	0.02 ± 0.09	0.80 ± 0.07	0.05 ± 0.09	3.12 ± 0.38	0.04 ± 0.07	4.92 ± 0.50

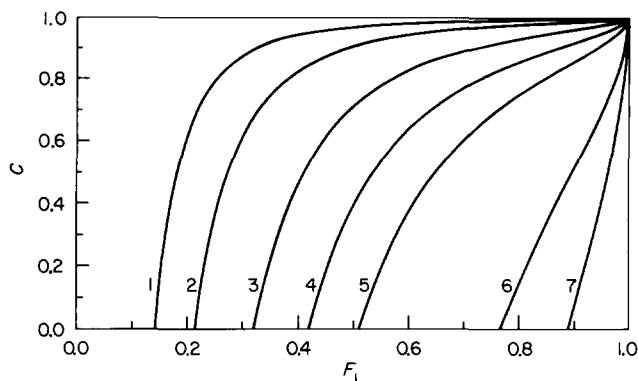


Figure 1 Fractional conversion (C) vs. instantaneous copolymer composition (mole fraction F_1 of VP) for the system VP/AMS. Curves 1–7 relate to initial feed compositions of VP (f_1) of 0.220, 0.325, 0.472, 0.594, 0.693, 0.894 and 0.957 respectively

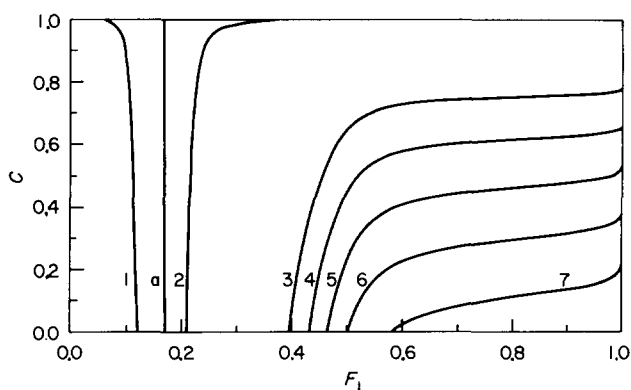


Figure 2 Fractional conversion (C) vs. instantaneous copolymer composition (mole fraction F_1 of VP) for the system VP/BA. Curves 1–7 relate to initial feed compositions of VP (f_1) of 0.112, 0.223, 0.584, 0.681, 0.775, 0.867 and 0.956 respectively. The curve denoted by a is for the azeotropic feed composition value of 0.165 for f_1

The value of 1.512, reported by Sedlaček and Dušek¹² as the n_D^{20} of poly-HEMA, refers to an unswollen gel, i.e. a lightly crosslinked material. The present measured value of 1.515 relates to linear polymer of high molar mass ($M = 6 \times 10^5 \text{ g mol}^{-1}$). Although the measured n_D^{20} for poly-VP was almost exactly the same, viz. 1.514, the material used was of a low nominal molar mass ($M = 4 \times 10^4 \text{ g mol}^{-1}$). Consequently, it was considered more legitimate to obviate any possible influence of molar mass on refractive index by measuring n_D^{20} for poly-VP of nominal molar mass $M = 7 \times 10^5 \text{ g mol}^{-1}$. The value was 1.522. Hence the two polymers are not almost exactly isorefractive as had appeared, but they and VP/HEMA copolymers of any composition do not differ in refractive index by more than 0.007.

The films A–F cast at 20°C were all clear and transparent. Each of the d.s.c. thermograms exhibited only a single T_g , the values for A–F being 98.5, 113, 118, 127, 135.5 and 169°C respectively with an uncertainty of $\pm 1^\circ\text{C}$.

DISCUSSION

The present results supplement the rather small number of reactivity ratios reported for copolymerizations involving VP. The uncertainties in r_1 and r_2 quoted¹³ for the latter are of a very similar magnitude to those found for the present four systems. In Table 2 it is seen that in each case $r_1 < r_2$. Moreover, since the product $r_1 r_2$ ranges

between 0.02 and 0.53, none of the systems exhibits ideal copolymerization. The VP/BA pair is the only system capable of affording copolymerization without change in composition. As indicated in equation (3) this occurs when $f_1 = 0.165$, this value being also the mole fraction of VP in the copolymer at all stages of conversion.

The Q – e scheme¹⁴ is sometimes adopted to predict the values of r_1 and r_2 , but it is accepted that this is at the most of only semi-quantitative utility. Thus this approach was adopted by us previously⁹ for the VP/BA system, prior to the present experimental determinations. The two values of r_1 were in good accord, but the actual experimental value of r_2 is now shown to be greater than the calculated one. On the basis of Q – e values we have calculated the following values of (r_1, r_2): VP/AMS (0.10, 7.66); VP/BA (0.02, 0.35); VP/HEMA (0.04, 4.37) and VP/MMS (0.04, 4.11). For the last three of these sets literature values¹⁵ of Q and e were used to calculate r_1 and r_2 . However no values of Q and e were available for AMS and recourse had to be made to the sole other relevant reactivity ratios available, viz. $r_1 = 0.86$ and $r_2 = 0.56$ for the system HEMA (1)/AMS (2). These gave $Q = 0.78$ and $e = -0.65$ for AMS and hence the calculated values cited above for r_1 and r_2 in the system VP/AMS. Clearly more reactivity ratios involving AMS are needed before one can assign definitive values to Q and e for this monomer. Apart from the VP/AMS pair the overall order of calculated r_1, r_2 values is in acceptable accord with that found experimentally.

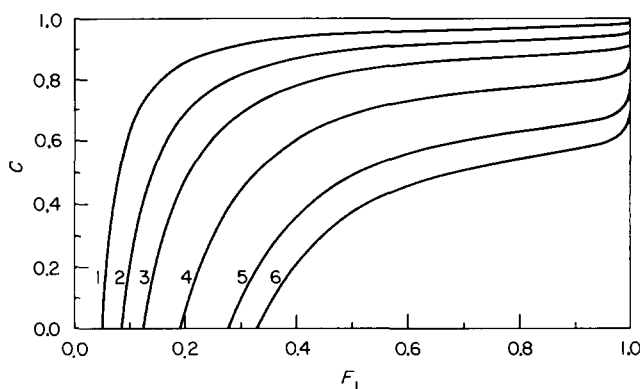


Figure 3 Fractional conversion (C) vs. instantaneous copolymer composition (mole fraction F_1 of VP) for the system VP/HEMA. Curves 1–6 relate to initial feed compositions of VP (f_1) of 0.145, 0.239, 0.333, 0.477, 0.631 and 0.707 respectively

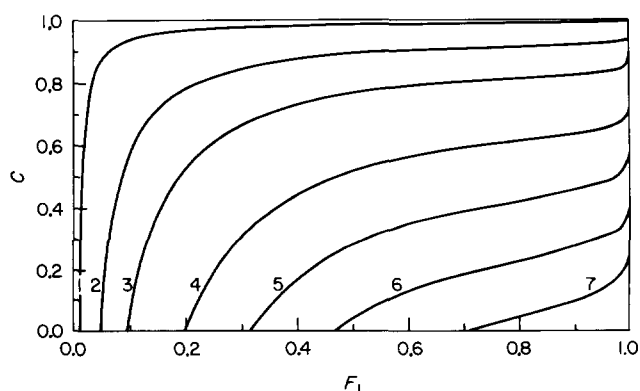


Figure 4 Fractional conversion (C) vs. instantaneous copolymer composition (mole fraction F_1 of VP) for the system VP/MMS. Curves 1–7 relate to initial feed composition of VP (f_1) of 0.043, 0.198, 0.357, 0.596, 0.769, 0.899 and 0.977 respectively

With regard to high conversion copolymerizations it is convenient to consider together the curves in Figures 1-4 with the observations on optical homogeneity of the copolymers produced (see Results section). Although the overall value of F_1 equals f_1 at high conversion, the immiscibility among constituent copolymers each of different composition can, in principle, lead to micro or macro phase separation and eventually opacity in the sample.

The closer the curves to the form of curve (a) in Figure 2, the more homogeneous is the sample with respect to composition. A wide change in F_1 is, of course, indicative of species encompassing a broad spread of composition. However, the conversion interval over which this occurs is also important. Thus, if it occurs at an essentially constant conversion or during a very small change in C , then the content of such heterogeneous material constitutes only a very small fraction by weight of the total.

On approaching $C = 1.0$ the slopes of the integral curves tend to values which can be finite, zero or infinite. When slopes at all stages of conversion are plotted vs. F_1 , the resultant differential distribution curves illustrate the fraction of final polymer which possesses a composition in each range. The general form can be readily visualized by inspection of the integral curves. The differential curves are not reproduced here, but the general form for two cases is shown schematically in Figure 5. One aspect is of major significance, viz. systems and initial feed compositions exhibiting an infinite slope at high conversion. These occur commonly in Figures 1-4, the instantaneous copolymer compositions in this region tending to $F_1 = 1$. Hence in this region, in addition to the other species present, the copolymer also comprises material which is nearly pure poly-VP. In general the larger is f_1 the lower is the conversion in the region of high conversion at which the slope tends markedly to infinity. These findings have been corroborated by analysis of the relative content of water extractable species within the high conversion copolymers.

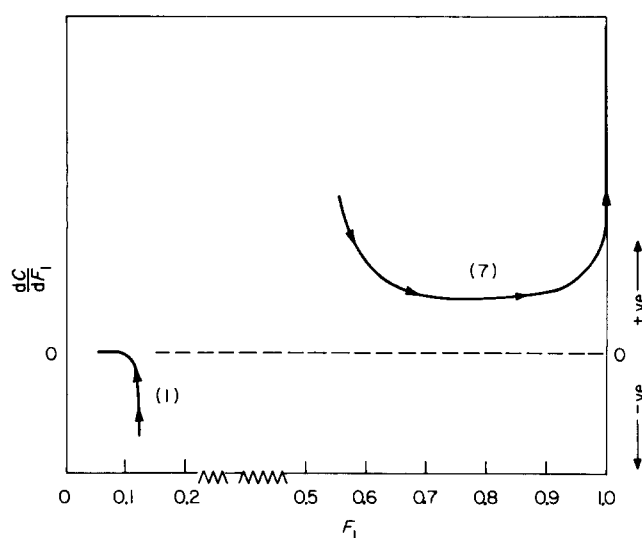


Figure 5 Schematic representation of differential compositional distribution curves. Curves (1) and (7) correspond to the integral distribution curves (1) and (7) respectively of Figure 2. Arrows indicate the direction of increasing conversion. At high conversion the slope tends to zero and F_1 to a small finite value in curve (1). In curve (7) the slope tends to infinity and F_1 to 1.0 at high conversion

Discussion of the VP/HEMA system will be deferred temporarily. On the basis of the aforementioned discussion the gradation in appearance from (c)→(o) (clear→opaque) for the other three systems can be rationalised qualitatively. It is somewhat surprising that optical clarity in the VP/BA system obtains for feed compositions not only in the vicinity of the azeotropic composition (curve (a) in Figure 2) but also as far from it as $f_1 = 0.584$ (curve 3 in Figure 2). This enhanced compatibility may possibly arise from γ -ray induced crosslinking of the more radiation sensitive component, BA, the content of BA in the copolymers over most of the conversion being greater than that in the feed. The very wide spread in F_1 at low f_1 compared with that at high f_1 in Figures 1 and 4 does not conflict with the observation that the copolymers produced at high f_1 are opaque. Curves 1 and 2 for example in these Figures illustrate only a moderate change in F_1 up to $\approx 70\%$ conversion and the larger spread in F_1 occurs over a rather small conversion interval. In contrast, curves 7 in both Figures show an immediate change in F_1 which continues up to high conversion with eventually an infinite slope.

The curves for VP/HEMA (Figure 3) are of a similar general form to those of Figures 1 and 4. At medium-high values of f_1 the heterogeneity is certainly large enough to indicate that the copolymer would be opaque. However, as indicated earlier, optical clarity is exhibited for this system at all feed compositions. It is emphasized that this system is in no way anomalous with regard to its compositional heterogeneity. The unusual feature is merely why this is not manifested visually.

The measured refractive indices show that, although the two homopolymers poly-VP and poly-HEMA are not exactly iso-refractive, their refractive indices are extremely close with the result that transparent films of their mixtures are produced. Incompatible polymers can form transparent films when both polymers have the same refractive index. However, transparent films formed from incompatible polymer will exhibit two glass transition temperatures characteristic of the components of the mixture, provided these two temperatures are sufficiently displaced from each other to be resolvable by the technique used for their detection¹⁶.

The d.s.c. technique used here gave a T_g for poly-HEMA which was in good agreement with the literature value¹⁷. For poly-VP values of T_g ranging from 54° – 175°C have been reported. Tan and Challa¹⁸ have collated these and have shown that the spread may be attributed to the influence of absorbed water and that a value close to the upper limit of this range represents the true T_g .¹⁸ The present value of 169°C , therefore, appears acceptable. On the basis of additivity (equation (4)), the T_g of a copolymer can be calculated

$$1/T_g = (W_1/T_{g1}) + (W_2/T_{g2}) \quad (4)$$

Copolymer (B) comprising a weight fraction 0.25 of VP and a weight fraction 0.75 of HEMA is thus calculated to have a T_g of 114°C , which compares well with the measured value of 113°C .

Finally, it is noted that the behaviour of the VP/HEMA system is consonant with the production of VP/HEMA copolymers and poly-VP-co-HEMA graft copolymers, which have been made as clear materials for subsequent biomedical applications as hydrogels^{19,20}.

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Note added in proof

Subsequent to the submission of this paper, determinations of reactivity ratios for the VP/HEMA system have been reported elsewhere (Reddy, B. S. R., Arshady, R. and George, M. H. *Eur. Polym. J.* 1985, **21**, 511). These authors obtained $r_1 = 0.06 \pm 0.10$ and 0.02 ± 0.14 via the Fineman–Ross and the Kelen–Tüdös methods, respectively and 4.35 ± 0.04 and 4.50 ± 0.24 for the corresponding values of r_2 .

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