

Observations on the homogeneity of cross-linked copolymers prepared by γ -irradiation

Malcolm B. Huglin and Mat B. Zakaria*

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

(Received 24 March 1983; revised 24 August 1983)

Bulk copolymerization *in vacuo* has been effected to 100% conversion via γ -irradiation. Visual assessment is made of the homogeneity of the products, which comprise n-butyl acrylate with *N*-vinyl-2-pyrrolidone over the whole composition range. Textural inhomogeneity (popcorn structure or spongy opacity), produced only below $\approx 5 \times 10^{-3}$ Mrad h⁻¹, is attributed to proliferous polymerization. At medium-high dose rates, the optical homogeneity, classified as opacity, translucency or transparency, is dictated only by the composition. Thus, transparency in a xerogel requires a minimum n-butyl acrylate content of 40 wt%, but the threshold composition is reduced by incorporating a hexa-functional crosslinking agent. There is a general trend towards decreased optical homogeneity on hydrating a xerogel to its hydrogel. The change in compositional distribution up to 100% conversion is analysed according to the procedure of Skeist and is shown to be consistent with the experimental observations on compatibility.

(Keywords: poly(n-butyl acrylate); poly(*N*-vinyl-2-pyrrolidone); 1,1,1-trimethylol-propane trimethacrylate; γ -irradiation; copolymer; homogeneity)

INTRODUCTION

A hydrogen can be defined as a crosslinked polymeric network containing a significant quantity of water (> $\approx 20\%$), but which does not dissolve in it. The unhydrated form is termed a xerogel. Much of the extensive literature on the preparation and properties of hydrogels is concerned with biomedical applications¹. The present authors are currently investigating polymers suitable for use as soft contact lens materials. In addition to the requirement of appreciable water content (vehicle for oxygen transport), this particular application demands high light transmission. Accordingly, attention has been focused on the conditions necessary to obtain materials which are optically clear not only as xerogels but also in the state of ultimate use, i.e. hydrogels.

The following abbreviations are adopted: BA, n-butyl acrylate; MMA, methyl methacrylate; PBA, poly(n-butyl acrylate); PVP poly(*N*-vinyl-2-pyrrolidone); TPT, 1,1,1-trimethylolpropane trimethacrylate; VP, *N*-vinyl-2-pyrrolidone.

As the copolymerizations are carried out to 100% conversion, the composition of the xerogel is the same as that of the initial feed mixture. The composition of the cross-linking agent TPT is based on the weight of the total constituents, whereas the composition of a monomer is based on the total weight of the monomers. For example, the notation BA30/VP70/TPT1 means a xerogel in which:

- BA comprises 30 wt% of (BA + VP)
- VP comprises 70 wt% of (BA + VP)
- TPT comprises 1 wt% of (BA + VP + TPT).

A temperature of 21°C applies throughout for the γ -

ray-induced copolymerization and for hydration of xerogels to hydrogels.

EXPERIMENTAL

Materials

BA (BDH), MMA (Hopkin and Williams) and VP (Aldrich Chem. Co.) were dried with anhydrous magnesium sulphate and vacuum distilled. TPT (ICN Pharmaceuticals Inc.) was used as received. Subsequent to this work an efficient chromatographic method of purifying TPT was devised². However, it was verified³ that, at the low concentrations of TPT used here, the properties of the copolymers were the same as those afforded by unpurified TPT. PBA was prepared by heating in an outgassed sealed ampoule a solution of BA in toluene (10% vol/vol) in the presence of lauroyl peroxide (1.22×10^{-3} mol l⁻¹) as initiator. After polymerization for 5 h at 65°C, the polymer was precipitated in methanol, centrifuged, washed and then dried *in vacuo* for 7 days at 35°C. The measured intrinsic viscosity of 0.254 dl g⁻¹ in acetone at 25°C, in conjunction with published Mark-Houwink constants⁴, yielded $\bar{M}_w = 57\,000$.

Procedures

Monomer mixtures were made up gravimetrically and outgassed by freeze-thaw cycles. The glass ampoules had been siliconized previously to facilitate subsequent removal of the solid rods of copolymer⁵. After sealing (≈ 0.001 Pa), the ampoules were subjected to a total dose of 1 Mrad of γ -irradiation from the ⁶⁰Co source at Salford University. Various dose rates, established by Fricke dosimetry, were used. It was established that 1 Mrad was sufficient to ensure 100% conversion and results appertaining to other aspects at higher total dose are excluded here.

* Present address: Jabatan Kimia, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia

Solid polymerized rods were removed, oven cured at 105°C for 24 h and cut into thin discs as described elsewhere⁵. Hydrogels were obtained by hydration in pure water to equilibrium swelling (≈ 7 days). Optical homogeneity was assessed visually. For one sample only (BA 30/VP 70/TPT 1) light transmittance of a polished disc was determined on a Unicam 1800 u.v. spectrophotometer coupled with a Unicam AR25 linear recorder. Optical densities were scanned between the wavelengths 380 to 700 nm.

RESULTS

Effect of radiation dose rate

For xerogel BA 30/VP 70/TPT 1 the appearance of the polymers produced at different dose rates is shown in Figure 1. It is evident that homogeneous xerogel is formed only at medium-high dose rate, the smallest dose rate to still retain homogeneity being 0.012 Mrad h⁻¹. However, this is not the critical minimum value (as discussed later).

All dose rates > 0.012 Mrad h⁻¹ give rise to materials which are both texturally and optically homogeneous (e.g. Figure 1a). Heterogeneity occurs below 0.012 Mrad h⁻¹. The heterogeneity is manifested by the presence of a popcorn structure within a homogeneous matrix (e.g. Figure 1b), which is discernible only because the matrix is transparent. The size of the popcorn domain increases with decreasing dose rate (Figures 1b and 1c). Indeed, at the lowest dose rate used, there is no homogeneous matrix at all and the material is porous and spongy (Figure 1d). The overall effect of dose rate on textural homogeneity is illustrated in Figure 2.

Role of feed composition

Effect of BA in BA/VP copolymers. At a total dose of 1 Mrad with a dose rate of 0.012 Mrad h⁻¹, a visual assessment of homogeneity was made on a series of BA/VP copolymers (in the absence of TPT) covering seventeen compositions within the range 0–100 wt% BA. Both homopolymers as well as copolymers comprising $> 40\%$ BA were transparent. The remaining compositions exhibited translucency except for the region 10–20% BA in which the xerogels were opaque. Examples of the three types of optical homogeneity are illustrated in Figure 3.

Hydration for 24 h afforded stable equilibrium degrees

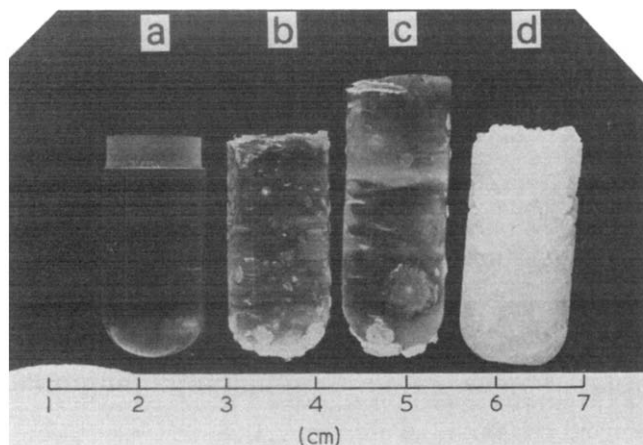


Figure 1 Development of textural inhomogeneity in BA30/VP70/TPT1 xerogels irradiated to a total dose of 1 Mrad at dose rates (Mrad h⁻¹) of (a) 0.012; (b) 0.0035; (c) 0.0011; and (d) 0.0004

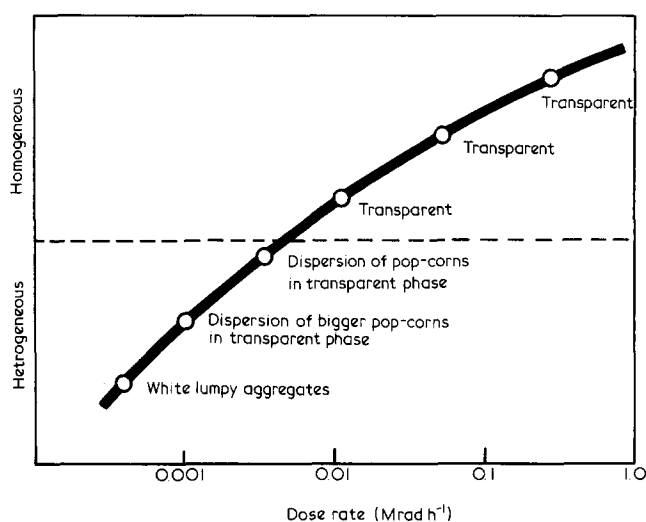


Figure 2 Influence of radiation dose rate on the optical and textural homogeneity of xerogel BA30/BP70/TPT1 (total dose=1 Mrad)

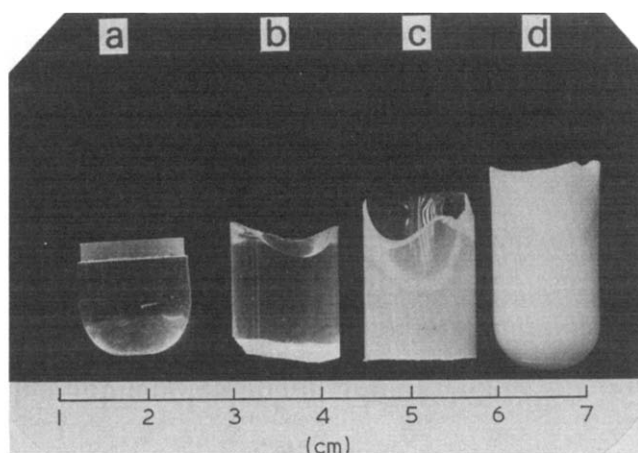


Figure 3 Photographs of four examples of xerogels prepared in the absence of TPT at a dose rate 0.012 Mrad h⁻¹ and a total dose of 1 Mrad. (a) 0% BA (transparent); (b) 100% BA (transparent); (c) 30% BA (translucent) and (d) 20% BA (opaque)

of swelling; full details are to be published. Here it is noted that these resultant hydrogels possess overall a reduced level of optical homogeneity at any composition. Thus, (a) both homopolymers as well as copolymers having $> 60\%$ BA were transparent; (b) the remaining compositions gave translucency, except for the extended region of 5–35% BA in which the hydrogels were opaque.

From these observations it is apparent that incompatibility ensues after the incorporation of only a very low content of hydrophobic BA into hydrophilic PVP. In contrast, incompatibility does not occur until the inclusion of VP into PBA attains a considerably higher value ($\approx 40\%$ VP and 60% VP in hydrogel and xerogel, respectively).

Effect of TPT in BA/VP/TPT copolymers. In addition to functioning as a cross-linking agent, TPT increased compatibility, yielding enhanced transparency for xerogels and hydrogels. The previously noted reduction in homogeneity induced by water is evident also when TPT is incorporated in the feed. As shown in Figure 4, the translucent xerogel BA 30/VP 70 requires only $\approx 0.1\%$ TPT for transparency and the opaque hydrogel requires

$\approx 0.25\%$ TPT. The minimum concentration of TPT needed to enhance optical homogeneity is not a fixed quantity, but increases with decreasing content of BA. Thus, for the initially opaque forms of BA 20/VP 80 xerogel and hydrogel, the curve (not illustrated) analogous to Figure 4 indicates the minimum concentrations of TPT necessary for transparency to be $\approx 0.5\%$ and $\approx 1.0\%$ in xerogel and hydrogel, respectively.

Effect of MMA in BA/VP/MMA terpolymers. It was indicated previously that, in the absence of TPT, neither the xerogel nor the hydrogel of BA 20/VP 80 was transparent. Transparency required much higher contents of BA. It was considered constructive to ascertain if transparency could be induced by maintaining the BA content at 20% but replacing parts of the residual 80% VP successively with a different hydrophobic monomer, MMA. Polymers of the following composition (BA/V-

P/MMA) were prepared: 20/80/0, 20/75/5, 20/70/10, 20/60/20, 20/50/30, 20/40/40 and 20/30/50.

The influence of MMA content on optical homogeneity is illustrated in Figure 5, which has two salient features, i.e. (1) transparent terpolymeric xerogels are obtainable provided the MMA content exceeds $\approx 15\%$ and (2) for the corresponding hydrogels none of the MMA contents is capable of producing transparency (30% MMA is a borderline situation in which the polymer is not unambiguously transparent).

Subsidiary results

Copolymerization of VP with PBA. The use of simultaneous interpenetrating networks and grafting has been reported in this field⁶. It was considered of interest to compare this technique with the present one. For BA 30/VP 70/TPT 1 both the xerogel and hydrogel are completely transparent (Figure 4). The feed mixture obtained by replacing BA with a PBA sample ($M_w = 5.7 \times 10^4$), i.e. PBA 30/VP 70/TPT 1, was completely clear. After the standard outgassing and irradiation procedure, reaction proceeded to 100% conversion. However, the product was completely opaque.

Light transmission. For a disc of xerogel BA 30/VP 70/TPT 1 (which was an optically homogeneous sample by visual assessment), the recorded optical density for a disc in its holder minus the value in the absence of the disc yielded the optical density (OD) of the xerogel. If I_t and I_0 are the intensities of transmitted and incident light respectively, then

$$10^{-OD} = I_t/I_0 = \text{transmittance}$$

At each of ≈ 20 selected wavelengths, OD was obtained and, hence, the transmittance, which was ≈ 0.81 ($\equiv 81\%$). Significantly smaller transmittance occurred only within 380–420 nm, presumably owing to absorption due to the pyrrolidone ring. It should be noted that transmission equals the sum of transmittance and surface reflection. Hence 81% represents a lower limit of the transmission.

DISCUSSION

Two types of homogeneity have been observed in this system, i.e. (a) optical and (b) textural. The former is influenced by the feed composition, whilst (b) has been shown to be affected by the radiation dose rate. At certain dose rates a composition, otherwise capable of producing an optically homogeneous xerogel, can lead to texturally heterogeneous copolymer. Thus, for optimization of conditions the dose rate effect must be elucidated prior to the influence of feed composition.

Textural homogeneity

For the single composition studied in this context (BA 30/VP 70/TPT 1) the marked difference in textural homogeneity between samples irradiated at dose rates ≥ 0.012 Mrad h^{-1} (homogeneous) and those irradiated at dose rates < 0.012 Mrad h^{-1} is indicative of a significant difference in the respective chain lengths formed. The phenomenon observed at very low dose rates is a typical example of the formation of proliferation (popcorn polymerization⁷), which prevails with acrylic-type monomers, where the solubility of the copolymer formed in the polymerizing medium is critically reduced at high chain

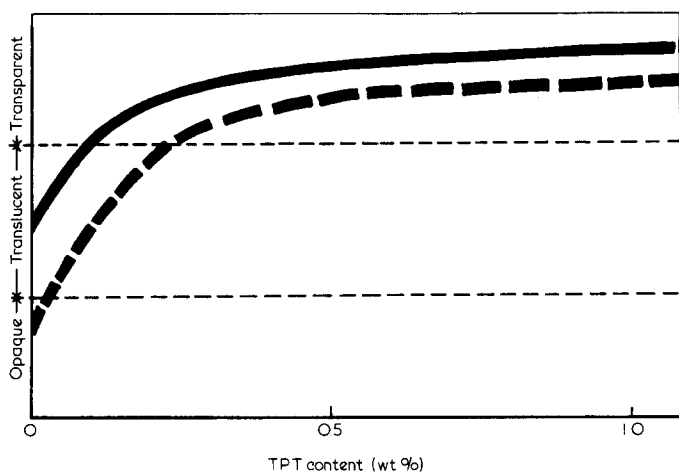


Figure 4 Influence of cross-linking agent on the optical homogeneity of BA30/VP70 xerogels (—) and hydrogels (---). Concentrations of TPT are 0, 0.05, 0.1, 0.185, 0.25, 0.38, 0.5 and 1.0 wt%. (Radiation conditions are as in Figure 3)

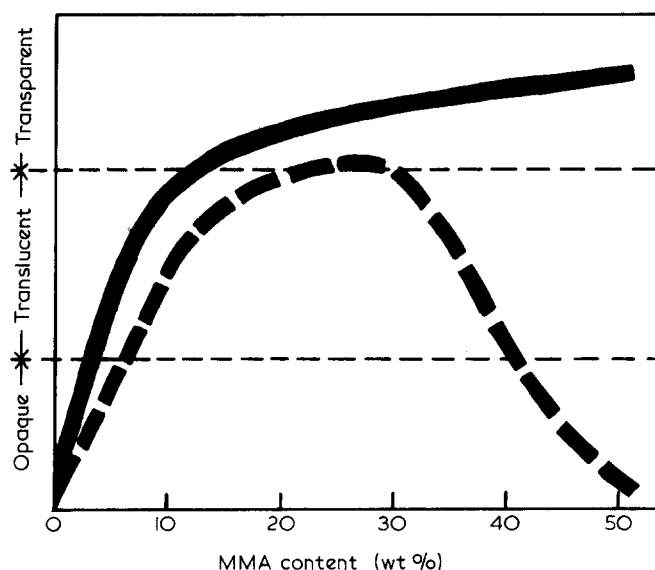


Figure 5 Effect of content of MMA on the optical homogeneity of BA20/VP/MMA xerogels (—) and hydrogels (---) prepared to a total dose of 1 Mrad at a dose rate of 0.012 Mrad h^{-1} . (Curves comprise 7 different compositions quoted in text encompassing the range 0% MMA – 50% MMA)

length. The insolubility arises as a result of the formation of very long chain polymer produced at low dose rates, the insoluble species acting as a nucleus for phase separation.

The copolymerization of the particular feed composition BA 30/VP 70/TPT 1 proceeds in such a way that the high molecular weight copolymer formed initially is richer in BA than is the feed. (See later for relevant details in terms of reactivity ratios). Hence, the residual monomer mixture is richer in VP. Insolubility is enhanced as copolymerization proceeds, for the high molecular weight copolymer with a large BA content does not dissolve or mix in a medium increasingly dissimilar to it (i.e. un-polymerized mixture enriched in VP). By this means prolific copolymerization proceeds to complete conversion producing samples of the type illustrated in Figures 1b, c and d. Branching, which is likely to occur in the BA part of the copolymer especially at high conversion, may also be a contributory factor in proliferation.

The need to use at least a certain lower limit of dose rate to obtain a texturally homogeneous product from the feed composition BA 30/VP 70/TPT 1 shows that a critical chain length exists, as kinetic chain length is inversely proportional to dose rate⁸. Of the dose rates used here the lowest one, at which texturally homogeneous xerogel was still produced, was 0.012 Mrad h⁻¹. However, the following evidence indicates that this does not represent the exact minimum value.

To assess the feasibility of large-scale preparations, the formation of a long rod (60 cm) was simulated by irradiating a series of short sample ampoules arranged vertically at various heights up to 60 cm above the normal source level, where the dose rate was 0.012 Mrad h⁻¹. Texturally homogeneous material was still obtainable at the highest position. At this position the dose rate was smallest, if a spherical envelope of radiation intensity is assumed. Applying the inverse square law of distance, the dose rate at this position is ≈ 0.005 Mrad h⁻¹. This appears to be a reasonable estimate, for at the lower dose rates of 0.0035 and 0.001 Mrad h⁻¹, the materials irradiated at normal source level were shown to be texturally heterogeneous (Figure 2).

These comments on popcorn formation relate to an effect which was unexpected, the overall aim being optimization of homogeneity. Consequently, further work involving different feed compositions at very low dose rate was not carried out. However, the previous arguments lead to the reasonable conjecture that prolific polymerization would be much less likely at very low dose rates, if the feed composition were much richer in BA (e.g. BA 80/VP 20/TPT 1). Under these conditions the similarity in compositions of copolymer and residual monomers would enhance miscibility, despite the large chain length.

Optical homogeneity

The occurrence of translucency or opacity in some of the xerogels suggests the existence of more than one species, i.e. at least two polymers which are immiscible. Such a possibility is plausible from the standpoint of the relative reactivities of the growing species. The authors have been unable to locate in the literature any experimental values of the reactivity ratios for the BA/VP pair (in this discussion subscripts 1 and 2 will relate to BA and VP, respectively). However, an estimate was made via the $Q-e$ scheme for which the relevant values have been

reported⁹. Thus, using $Q_1 = 0.51$ and $e_1 = 1.02$, a value of $r_1 = 0.40$ is calculated for BA. For VP a value of $r_2 = 0.023$ is obtained similarly from $Q_2 = 0.14$ and $e_2 = -1.14$. With these values of r_1 and r_2 the variation of mol fraction F_1 of BA in copolymer with mole fraction f_1 of BA in the feed at low conversion is given by the following form of the copolymer-composition equation¹⁰:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \quad (1)$$

The plot of F_1 versus f_1 calculated from equation (1) relates to instantaneous compositions only, i.e. low conversion. This curve, which is not reproduced here, shows that (a) for $f_1 = 0-0.62$ (the azeotropic composition), $F_1 > f_1$ and (b) for $f_1 = 0.62-1.0$, $F_1 < f_1$. Because of the similar molecular weights of BA and VP, the molar compositions here are close to the weight compositions used and quoted in the bulk of this text, e.g. for BA20/VP80, the weight fraction of BA is 0.20. The actual value of $f_1 = 0.199$. Similarly for BA30/VP70 and BA80/VP20 the values of f_1 are 0.271 and 0.776, respectively.

However, during copolymerization the values of f_1 and F_1 alter to an extent depending on r_1 and r_2 . For BA20/VP80 the initial F_1 is ≈ 0.50 , but this value decreases with increasing conversion. In contrast, for BA80/VP20 the initial $F_1 = 0.72$ and in this case F_1 increases with conversion.

The distribution of composition according to conversion has been analysed by Skeist¹¹. A brief outline only is presented here and reference should be made to the original paper for full details. It is shown that between two successive stages of conversion, i and j , the compositions of copolymer and feed mixture change by amounts $\Delta F_1 (= F_{1,j} - F_{1,i})$ and $\Delta f_1 (= f_{1,j} - f_{1,i})$, respectively. Also equation (2) is applicable:

$$\ln\left(\frac{M}{M_0}\right) = \int_{f_{1,i}}^{f_{1,j}} \frac{df_1}{F_1 - f_1} \quad (2)$$

Starting with initial conditions at zero conversion (i.e. $i \equiv 0$), the corresponding F_1 is calculated from equation (1). Taking a small change $\Delta f_1 = 0.01$ the quantities of unreacted monomers are calculated and thence the value of ΔF_1 . The procedure is repeated for successive changes of $\Delta f_1 = 0.01$. In the plot of $1/(F_1 - f_1)$ versus f_1 , the area A of each portion separated by Δf_1 is obtained. From equation (2) it is evident that A represents the value of $\ln(M/M_0)$, where M and M_0 are the molar concentrations of total monomers at conversion intervals j and i , respectively. As $M < M_0$, it follows that $A = -\ln(M/M_0)$. Hence, from equation (2), the conversion (expressed as a fraction) is given by:

$$\text{Conversion} = 1 - e^{-A}$$

F_1 is calculated as indicated for each A , thereby giving the conversion throughout the particular i,j interval. The process is continued until the cumulative sum of each conversion interval attains unity.

The final result of this rather long analysis is given here for two extreme cases of especial relevance, i.e. BA20/VP80 (Figure 6a) and BA80/VP20 (Figure 6b). In

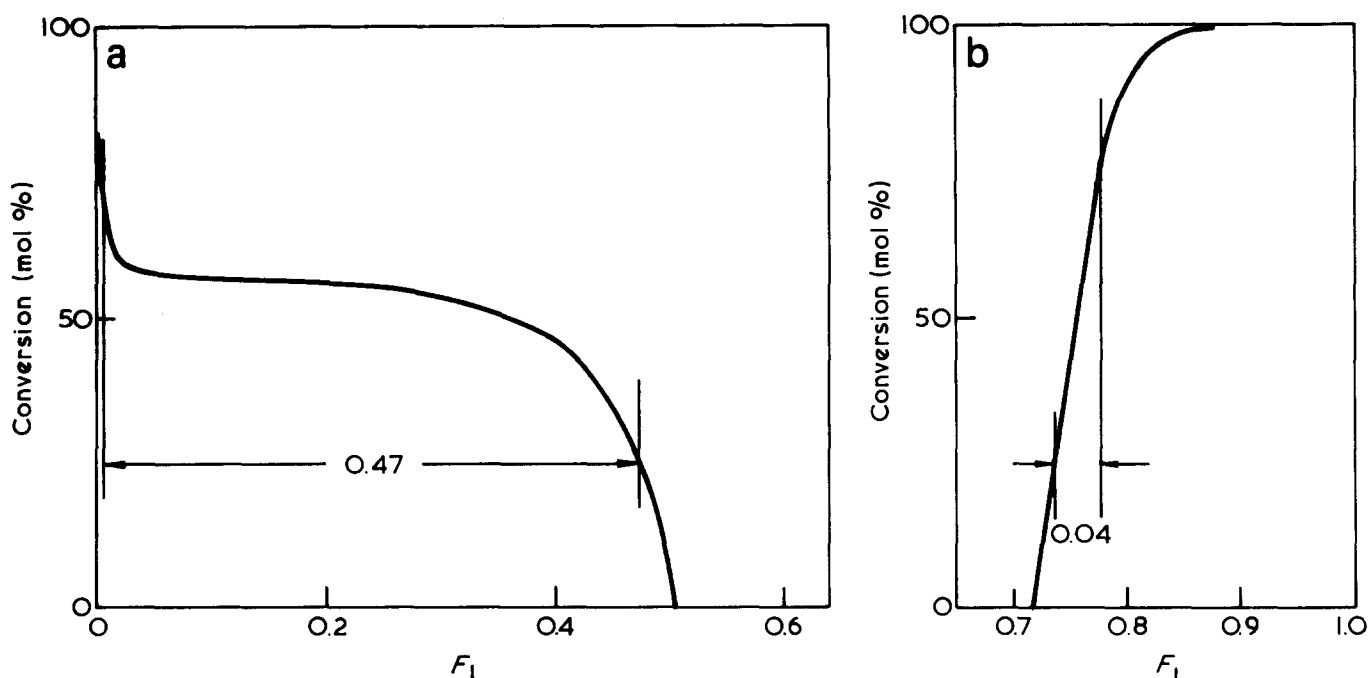


Figure 6 Integral distribution of copolymer composition with conversion for initial feed compositions of (a) $f_1 = 0.199$ (20 wt% BA) and (b) $f_1 = 0.776$ (80 wt% BA). The numbers indicate ΔF_1 for the interquartile 25–75% conversion and F_1 is the mol fraction of BA in the copolymer

the former, the copolymer composition is relatively constant up to $\approx 45\%$ conversion, i.e. F_1 varies from ≈ 0.5 to ≈ 0.4 . Thereafter, from 45 to 60% conversion, F_1 decreases markedly from ≈ 0.4 to ≈ 0.02 . Up to 60% conversion the compositional heterogeneity is sufficient to cause incompatibility. The value of 0.47 indicated for ΔF_1 over the interquartile 25–75% conversion is extremely large. Figure 6a also shows that 100% conversion is approached asymptotically, i.e. the slope in this region is infinite. Hence, in the region of 100% conversion there is an appreciable quantity of copolymer comprising almost pure PVP. The experimental observation, that the xerogel BA20/VP80 is opaque, is entirely consistent with the broad compositional distribution.

A different situation obtains for BA80/VP20 (Figure 6b). Over the whole range of conversion, F_1 increases by only 0.12, i.e. from 0.72 initially to 0.84 finally. Moreover the interquartile for 25–75% conversion corresponds to a change in F_1 of only 0.04. Complete conversion is approached with a zero slope and at 100% conversion there is no pure PBA (of $F_1 = 1$). As $F_1 = 0.84$ here, there is no pure PVP either (of $F_1 = 0$). Thus, overall the copolymer is homogeneous in composition, which is consistent with the observed transparent nature of xerogel BA80/VP20.

Other aspects

Incorporation of a crosslinking agent as an ultimate means of forcing compatibility between existing polymer chains is well established⁶. The same situation obtains here with the additional factor that TPT is a hexafunctional methacrylate, which participates in the terpolymerization. As TPT is more structurally akin to BA than to VP, it is reasonable that (1) the opacity in xerogel BA20/VP80, for example, becomes transparency if 0.5% TPT is incorporated and (2) the quantity of TPT required for this enhancement in optical homogeneity decreases with increasing BA content.

The composition PBA30/VP70/TPT1, however, produces an opaque xerogel, despite the inclusion of 1% TPT. Here, one of the components is a preformed polymer (PBA) and the possible processes differ from those which produce the transparent xerogel BA30/VP70/TPT1, i.e. (1) TPT cannot participate in direct terpolymerization because one of the components is a polymer rather than a monomer; (2) because it approaches the maximum of compositional heterogeneity, the mixing is unfavourable between PBA and a branched or crosslinked copolymer, which necessarily comprises almost pure PVP; (3) the high G (radical) values of polyacrylates indicate that grafting of VP will occur to the PBA backbone. Hence, overall miscibility is required among at least three species, i.e. graft copolymer¹², ungrafted PBA¹³ and homopolymer of PVP produced by direct irradiation. Accordingly, it is perhaps not surprising that the product is opaque, even without involving additional constraints of chain length dependence of miscibility.

From the standpoint of ultimate end-use, optical homogeneity in the hydrogel form is of prime importance. It has been noted that, for a particular composition, homogeneity in a hydrogel is rather less than in the corresponding xerogel. Thus, for BA50/VP50 the xerogel is transparent but the hydrogel is translucent. Similarly, for BA30/VP70 the xerogel is translucent, whereas the hydrogel is opaque. As PBA is immiscible with water, the hydration process involves hydrogen bonding with the VP moieties in the copolymer. Any existing state of miscibility within the xerogel is thereby disrupted by chain expansion of PVP regions only, coupled with the plasticizing effect of water which weakens the overall inter-chain interactions. The observed phase separation in samples of high VP content accords with the observed increase of total water content with increasing content of VP³ (the behaviour might be different if water were replaced by a non-polar liquid such as toluene, which has a high affinity for the BA moieties).

When VP is replaced partially by MMA in a xerogel there is enhanced optical homogeneity (Figure 5), the behaviour thus being equivalent to simply increasing the BA content (see previously). As before, the hydrogel is of lower homogeneity than the xerogel at each composition. However, at high (30–50%) MMA contents, the decrease is exceptionally marked in the respect that opacity is produced for compositions anticipated (see previously) to afford transparency. A satisfactory quantitative explanation for this finding is yet to be provided, but the following qualitative considerations are relevant:

(1) BA70/VP30 and BA20/MMA50/VP30 have the same VP contents, but the former hydrogel is transparent and the latter opaque. Moreover, the total % swelling in water of the former ($\approx 10\%$) is significantly less than that of BA20/MMA50/VP30 ($\approx 20\%$)³. It is established¹⁴ that the fraction of bound water is larger the smaller is the total water content. Consequently, it is inferred that BA20/MMA50/VP30 has the lower fraction of bound water leaving a large fraction (out of the 20%) available as free water. This free water can then participate in self-structuring or microsineresis, the separate phase manifesting itself by opacity.

(2) Considering the same examples as in (1), the overall miscibility or homogeneity is dependent on the energy of several types of interaction. Of these, the ones involving VP are VP–VP, VP–BA, VP–water, which are augmented by VP–MMA in the case of BA20/MMA50/VP30 (optically homogeneous crosslinked VP/MMA copolymers have been used commercially as soft contact lens materials¹⁵). As swelling involves VP moieties and higher swelling is exhibited by the MMA-containing polymer, less of the total 30% VP becomes available to participate in the remaining types of interaction, which are necessary for overall miscibility. Consequently the hydrogel of BA20/MMA50/VP30 is opaque.

In conclusion, conditions for optimizing homogeneity in BA/VP xerogels and hydrogels have been obtained.

With chemical free radical initiators, the low mobility of residual monomer at high conversion leads to dead-end polymerization. Continuous γ -irradiation has been shown to afford an excellent means of attaining 100% conversion.

ACKNOWLEDGEMENTS

One of the authors (MBZ) gratefully acknowledges financial support from Universiti Kebangsaan, Malaysia, provided under the aegis of its Staff Training Programme.

REFERENCES

- 1 Pedley, D. G., Kelly, P. J. and Tighe, B. J. *Brit. Polym. J.* 1980, **12**, 99
- 2 Huglin, M. B., Yahya, I. B. and Zakaria, M. B. *Polymer* 1982, **23**, 340
- 3 Zakaria, M. B. *Ph.D. Thesis* University of Salford, 1983
- 4 Kurata, M., Tsunashima, Y., Iwama, M. and Kamada, K. in 'Polymer Handbook', 2nd edn., (Eds. J. Brandrup and E. H. Immergut), Interscience, New York, 1975, pp IV-1
- 5 Huglin, M. B. and Zakaria, M. B. *J. Appl. Polym. Sci.* 1983, **28**, 2451
- 6 Olabisi, O., Robeson, L. M. and Shaw, M. T. 'Polymer–Polymer Miscibility' Academic Press, 1979, p. 262
- 7 Breitenbach, J. W. in 'Encyclopedia of Polymer Science and Technology', (Ed. N. M. Bikales), Interscience, New York, 1969, Vol. 11, p. 587
- 8 Wilson, J. E. 'Radiation Chemistry of Monomers, Polymers and Plastics', Marcel Dekker, Inc., New York, 1974, p. 269
- 9 Young, L. J. *J. Polym. Sci.* 1961, **54**, 411
- 10 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, N.Y., 1953, p. 180
- 11 Skeist, I. *J. Am. Chem. Soc.* 1946, **48**, 1781
- 12 Huglin, M. B. and Richards, R. W. *J. Appl. Polym. Sci.* 1980, **25**, 2513
- 13 Collins, R., Huglin, M. B. and Richards, R. W. *Eur. Polym. J.* 1975, **11**, 197
- 14 Lee, H. B., Jhon, M. S. and Andrade, J. D. *J. Colloid Interface Sci.* 1975, **51**, 225
- 15 Cordrey, P. W., Frankland, J. D. and Highgate, D. J. U.K. Patent 1,439,132 (1976)