Registry No. (Styrene)(isoprene) (block copolymer), 105729-79-1.

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(31) This may be due to the corrections to the mean field value of $\chi_{eff} = \chi\phi_p$. The detailed analyses on the corrections will be deferred until we get precise values for χ_{1s} and χ_{2s}, the χ-parameters between the polymers and solvent. However, if $\chi_{1s} \simeq \chi_{2s} \simeq 0.45$, as in the case of polystyrene/polyisoprene/toluene, $\phi_p = 0.6–0.8 \gg f_0 = (1 - 2\chi_{1s})/u^* \simeq 0.02$, so that the block copolymer solutions are in θ state. Further $\phi_p \gg \chi_{12}/u_{12}^* = 0.01–0.5$, so that the renormalization group effect is expected to be small (see ref 23 for details). In this case we expect the mean field value of $\chi_{eff} = \chi\phi_p$ is correct.

(32) Subsidiary maxima that are weak but occasionally seen in the profiles at $T \geq 120$ °C (part b, Figure 1) are not reproducible and should be regarded as artifacts. However, the maxima in the profiles at lower temperatures, $T \leq 100$ °C (part a, Figure 1), marked by arrows are reproducible.

(33) Close observation of the results in Figures 3 and 6, some data especially those for n = 8 and 18, tend to show a tendency of decreasing D_{dis} with increasing T. However, it is difficult to claim positively that D_{dis} decreases with T within experimental accuracy. Within experimental accuracy and judging from the data for all n, it is fair to say that D_{dis} is independent of T. There appear to be more important discussions here. That is, as we pointed out previously,[18] it is difficult to decide unequivocally at present whether the transition between the ordered state (D_{ord} being temperature dependent) and the disordered state (D_{dis} being temperature independent) is sharp or gradual. Here we take a simplified picture, i.e., the sharp transition as a starting step.

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Studies on Copolymeric Hydrogels of *N*-Vinyl-2-pyrrolidone with 2-Hydroxyethyl Methacrylate

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ABSTRACT: *N*-Vinyl-2-pyrrolidone and 2-hydroxyethyl methacrylate in both the absence and the presence of ethylene glycol dimethacrylate have been copolymerized to high conversion by γ-irradiation. The resultant xerogels were swollen to equilibrium in water to yield hydrogels. The effects of monomer composition and concentration of added cross-linking agent on the swelling behavior and mechanical properties of these hydrogels at 294 K were investigated, the latter involving measurements of stress (compression)–strain. The findings were interpreted on the basis of terpolymer compositional drift as predicted by the *Q–e* scheme. Inhomogeneous cross-linking of the copolymer network was noted particularly at high contents of *N*-vinyl-2-pyrrolidone.

Introduction

The following abbreviations are adopted in the text: BA, *n*-butyl acrylate; EDMA, ethylene glycol dimethacrylate; EWC, equilibrium water content (=wt % water in hydrogel at equilibrium); HEMA, 2-hydroxyethyl methacrylate; VP, *N*-vinyl-2-pyrrolidone; TPT, 1,1,1-trimethylolpropane trimethacrylate. In addition, the polymeric form is prefixed where appropriate by P-.

In the authors' laboratory recent studies have been devoted to uniaxial compression and swelling measurements

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on hydrogels of (a) P-HEMA,[1] (b) P(VP-*co*-EDMA),[2] and (c) P(BA-*co*-VP-*co*-TPT).[3,4] In (a) there are both hydrophilic and hydrophobic characteristics and the EWC is only moderately large (~40 wt %).[1,5,6] The EWC is relatively insensitive to added cross-linker and is only reduced significantly when the latter is introduced at a very high concentration. The same considerations regarding cross-linking agent apply to (b), but in this highly hydrophilic polymer the EWC in the absence of cross-linker is very large (~95 wt %).[2] In (c) the presence of the hydrophobic comonomer BA affords an extremely wide range of EWC values, an effect which is more pronounced than that induced by variations in the content of the cross-linking agent TPT.[3,4] Nonetheless, the level of cross-linking is a property of a hydrogel, which is of comparable importance to its overall EWC because of its influence on the elastic modulus.

The system examined in the present work combines features of systems (a)-(c) and is focused on hydrogels of P(VP-*co*-HEMA) in which the parent xerogels are prepared in the absence and presence of EDMA. In the latter instance the synthesis of the xerogel constitutes a terpolymerization. We have demonstrated recently[2] that inhomogeneous cross-linking occurs, when VP is polymerized in the presence of EDMA during the copolymerization on account of the disparate reactivities of VP and EDMA, and this drift was shown to affect adversely the properties exhibited subsequently by the swollen gels. The intention here is to extend this form of investigation to the terpolymer system in which VP and EDMA are retained and with HEMA included as the third comonomer.

A temperature of 294 K applies to swelling and compression measurements as well as to the polymerization by γ-irradiation. Compositions are expressed as percentage by weight. For example, the designation HEMA30/VP70 means that EDMA is absent and that HEMA/VP is 30/70 (w/w). The same ratio of HEMA to VP obtains in a terpolymer designated as HEMA30/VP70/EDMA1. However, here EDMA comprises 1 wt % of the total monomers (HEMA + VP + EDMA). Because copolymerization and terpolymerization were conducted to very high conversion, these designations apply equally to the initial feed composition and to the total overall composition of polymer.

Experimental Section

Materials. VP (Aldrich Chemical Co.) and HEMA (Sigma Chemical Co.) were purified as described previously.[7,8] EDMA (Ancomer, TM3) was purified by column chromatography with silica gel as absorbent and *n*-hexane/diethyl ether (7/3 v/v) as eluant. Deionized water was used as the swelling medium.

Polymerization. The procedures for the polymerization and post-treatment of resultant xerogels have already been described fully elsewhere[3,9-11] and the following brief details only are given here. Monomer mixtures, made up gravimetrically, were outgassed in cylindrical, siliconized[10] glass ampules, which were sealed (10^{-4} mmHg) and subjected to γ-irradiation to a total dose of 1 Mrad at a dose rate of 0.01 Mrad h^{-1} as determined by Fricke dosimetry. The solid rods of polymer were then oven cured for 24 h at 378 K. From the small loss in weight on oven curing the conversion was found to be always in excess of 98 wt %.

Swelling. The polymer rods were turned on a lathe to produce xerogel disks (diameter ~8 mm, thickness ~1 mm) and cylindrical pellets (diameter ~8 mm, thickness ~8 mm). Each sample was weighed, and its dimensions were measured with a micrometer gauge. Samples were immersed in water, which was changed regularly to allow removal of any sol fraction. Equilibrium swelling times were 2-3 weeks and 8-12 weeks for disks and pellets, respectively, these times representing those for the swollen gels to attain constant weight. The dimensions of the swollen gels were measured using either calipers or a cathetometer. The volume fraction ϕ_2 of polymer in the hydrogel was obtained from the measured diameters of dry (d_0) and swollen (d) polymer; viz., $\phi_2 = (d_0/d)^3$.

Table I
Water Contents at 294 K and Sol Fractions for P(HEMA-*co*-VP) Hydrogels of Different Compositions Prepared in the Absence of EDMA

xerogel	sol fractn, wt %	EWC, wt %	ϕ_2	$\phi_2{}^{*a}$
HEMA95/VP5	7.4	40.4	0.537	0.567
HEMA90/VP10	11.2	42.4	0.515	0.559
HEMA85/VP15	14.4	44.1	0.497	0.556
HEMA80/VP20	15.1	45.9	0.479	0.552
HEMA75/VP25	18.5	48.7	0.454	0.550
HEMA70/VP30	18.1	50.2	0.438	0.543
HEMA50/VP50	26.2	67.8	0.272	0.393
HEMA40/VP60	28.1	77.5	0.187	0.291
HEMA30/VP70	32.4	85.4	0.119	0.213

[a] $\phi_2{}^*$ denotes the volume fraction of polymer uncorrected for extracted sol during swelling, and ϕ_2 is the corrected value.

Some comment is relevant here on the determination of the volume fraction of polymer. Because of the finite sol fraction extracted during swelling, the value of d_0 used to calculate this volume fraction is in error and the latter is consequently overestimated. The volume fraction of polymer, which is obtained directly from measured dimensions is an incorrect or apparent one, $\phi_2{}^*$. In principle, the true value of d_0 could have been measured on the pure sol-free xerogel after drying the swollen hydrogel. Although the mass m_2 of pure xerogel after drying could be obtained, it proved difficult to measure the diameter on account of some distortion of the disks on drying, especially for samples of significant sol fraction. To obtain the correct volume fraction of sol-free polymer in hydrogel at equilibrium, ϕ_2, the following procedure was adopted.

(a) The density of sol-free xerogel ρ_2 was calculated from the following expression in which $\rho_{\text{P-VP}}$ is the density of P-VP homopolymer and $\rho_2{}^*$ is the density of xerogel obtained from the mass and measured dimensions prior to swelling

$$(1/\rho_2{}^*) = (1/\rho_2)(1 - \text{sol fraction}) + (1/\rho_{\text{P-VP}})(\text{sol fraction})$$

The assumption is made here that the sol fraction approximates in composition to that of P-VP (see also Results).

(b) The corrected volume fraction ϕ_2 of polymer in hydrogel is then calculated from the following expression in which ρ_1 is the density of water and m is the mass of sol-free hydrogel at swelling equilibrium

$$\phi_2 = (m_2/\rho_2)/[(m_2/\rho_2) + (m - m_2)/\rho_1]$$

Values of parameters listed later, which depend on volume fraction of polymer, have been obtained via the use of corrected values, ϕ_2. These are also listed. In order to indicate the order of error incurred by failure to allow for extracted sol fraction, we have also listed, for comparison, the uncorrected volume fractions, $\phi_2{}^*$.

Uniaxial Compression. Full details are presented in a previous paper[2] of a compression rig, which was constructed here and used successfully in our studies on other hydrogels.[1-4] The same apparatus was employed here on swollen P(VP-*co*-HEMA) and swollen P(VP-*co*-HEMA-*co*-EDMA) pellets, which were maintained in a thermostated bath containing deionized water throughout the measurements.

Results

For samples prepared in the absence of EDMA, the copolymer composition was varied over a wide range and the effect on swelling is given in Table I. With increasing content of VP, the EWC and sol fraction both increase. In an earlier report[7] on the HEMA(1)/VP(2) copolymerization involving calculation of compositional heterogeneity via a form of the Skeist procedure,[12] a plot was given of fractional conversion vs instantaneous composition as expressed by the mole fraction of VP in the

Table II
Water Contents at 294 K and Sol Fractions for P(HEMA-*co*-VP-*co*-EDMA) Hydrogels Prepared in the Presence of Different Concentrations of EDMA but at a Fixed Composition of HEMA and VP

xerogel	sol fractn, wt %	EWC, wt %	ϕ_2	ϕ_2*
HEMA70/VP30/EDMA0.25	17.6	46.8	0.471	0.545
HEMA70/VP30/EDMA0.50	17.8	46.7	0.473	0.565
HEMA70/VP30/EDMA0.75	16.8	46.1	0.479	0.574
HEMA70/VP30/EDMA1	16.5	45.5	0.484	0.578
HEMA70/VP30/EDMA2	18.3	45.5	0.484	0.578
HEMA70/VP30/EDMA3	14.7	42.3	0.517	0.606
HEMA70/VP30/EDMA4	12.5	40.3	0.538	0.625
HEMA70/VP30/EDMA5	12.9	38.4	0.558	0.649

[a] ϕ_2* denotes the volume fraction of polymer uncorrected for extracted sol during swelling, and ϕ_2 is the corrected value.

Table III
Properties Obtained from Compression–Strain Measurements at 294 K for P(HEMA-*co*-VP) Hydrogels of Different Compositions Prepared in the Absence of EDMA

xerogel	E, MN m^{-2}	ν_e, mol dm^{-3}	M_c, kg mol^{-1}	χ
HEMA95/VP5	0.813	0.109	11.7	0.804
HEMA90/VP10	0.550	0.077	16.6	0.784
HEMA80/VP20	0.487	0.067	19.1	0.751
HEMA70/VP30	0.372	0.059	21.6	0.718
HEMA50/VP50	0.229	0.033	38.5	0.610
HEMA40/VP60	0.083	0.014	90.4	0.569

copolymer. This demonstrated that, because HEMA is the more reactive of the two comonomers, it enters the copolymer more quickly than VP does. Hence, in the later stages of conversion, the product has a composition very close to that of P-VP homopolymer. The higher the VP content in the feed, the lower the conversion at which HEMA is totally consumed. We have not determined the sol fraction at low or medium conversion, but the increasing order of sol fractions in Table I for high-conversion products accords with the theoretical predictions. The chemical nature of the sol fraction was not verified experimentally, but, because P-HEMA is insoluble in water, it is reasonably assumed to be P-VP and/or P(VP-*co*-HEMA) of very high VP content (by analogy with the comparable situation in P(VA-*co*-VP) hydrogels for which the nature of the sol fraction was verified experimentally).[11] At still higher contents of VP in the feed and xerogel, theory predicts a continual increase in sol fraction. Although samples containing >70 wt % VP were prepared, their characteristics are not included in Table I, because these gels disintegrated during the swelling process. The copolymers considered so far were prepared in the absence of EDMA and so owe their structure on swelling to light cross-linking by γ-radiation during the preparation as well as to physical hydrophobic interactions imparted by the HEMA component. For a copolymer cross-linked with 0.5 mol % EDMA (corresponding to HEMA40/VP60/EDMA0.84 in the designation adopted here), Patel has reported[13] an EWC of 72 wt %, which may be compared with a rather higher value of 77.5% obtained here for the same copolymer prepared in the absence of cross-linker.

An attempt was made here to study the effect of concentration of cross-linker at two specific compositions representing high and low contents of VP, viz. (a) HEMA30/VP70 and (b) HEMA70/VP30. In the preparations EDMA was used at several concentrations within the range 0.25–5.0 wt %. In set (a) the samples all disintegrated during swelling. The situation is similar in effect to, but probably different in origin from, that obtained for the swelling of cross-linked poly(methacrylic acid) in water, in which system the gels disintegrated at high degrees of neutralization and the osmotic or electrostatic forces were large enough to induce chemical bond rupture.[14,15] We have been unable to explain adequately the large physical stresses produced during swelling for set (a). They may well be associated with inhomogeneity with respect to separation of hydrophilic and hydrophobic domains within the gel. Results for set (b) are given in Table II. The sol fraction is seen to decrease with increasing content of EDMA but, even on incorporating 5 wt % EDMA, the sol fraction remains significant. The EWC and the corresponding volumetric water content, $1 - \phi_2$, both decrease with increase in EDMA content, but this decrease is a relatively small one.

Compression–Strain. Relevant equations and their utilization to yield network parameters have been described in detail previously.[3] Essentially, on the basis of the Flory–Huggins–Rehner theory, a knowledge of ϕ_2, the molar volume V_1 of swelling liquid, and the effective cross-linking density ν_e allows one to derive the polymer–liquid interaction parameter χ. The value of V_1 for water was taken [16] as 18.04×10^{-3} dm^3 mol^{-1}. Young's moduli E of the hydrogels were obtained as the slopes of linear plots of stress vs strain, where the stress is the applied compressive force per unit area of swollen gel and the strain is $(\lambda - 1)$, where λ denotes the ratio of the deformed to undeformed lengths of swollen pellet. Values of ν_e were obtained from the slopes of plots of τ vs $(\lambda - \lambda^{-2})$ according to eq 1[17] in which RT has its normal meaning and τ is the

$$\tau = RT\nu_e\phi_2^{-1/3}(\lambda - \lambda^{-2}) \qquad (1)$$

applied compressive force per unit area of dry xerogel. Examples of such linear plots have been given previously for P(BA-*co*-VP-*co*-TPT),[3,4] P(VP-*co*-EDMA),[2] and P-HEMA hydrogels,[1] and hence those obtained for the present system are not reproduced here.

Densities of the xerogels were determined as already indicated earlier in the text. The ratio of density to ν_e equals the molar mass between cross-links, M_c. The derived values of E, ν_e, M_c, and χ are listed in Table III for P(HEMA-*co*-VP) copolymers of six different compositions all prepared in the absence of cross-linking agent. The decrease in χ with increasing content of VP is consistent with the insolubility and solubility in water of P-HEMA and P-VP, respectively. Increasing content of VP is also accompanied by a fall in E and ν_e. This is accountable on the basis of a decrease in physical cross-linking (hydrophobic bonding) as the content of HEMA decreases; it has been shown previously[1] that the hydrophobic bonding in P-HEMA makes a contribution to the measured elastic modulus of the network.

For the copolymers of one fixed composition (70 wt % HEMA) prepared in the presence of six different concentrations of EDMA, the derived values of E, ν_e, χ, and M_c are given in Table IV. As anticipated for normal network behavior, the first two of these quantities increase with increasing level of cross-linking agent. Because $M_c \propto 1/\nu_e$, the values of M_c follow the reverse sequence. The uncross-linked copolymer HEMA70/VP30 is itself insoluble in water. Further reduced polymer–water interaction on introducing cross-linking is evidenced by the increase in χ with increasing concentration of EDMA.

From the molar mass of EDMA and the densities of the xerogels, the concentrations of EDMA (wt %) were converted to the theoretical cross-linking densities ν_t (mol dm^{-3}). Except at the highest content of EDMA used, the effective cross-linking densities (ν_e in Table IV) exceeded ν_t. The variation of ν_e with ν_t is illustrated in Figure 1. Least-squares analysis (correlation coefficient 0.968) gives

Table IV
Properties Obtained from Compression–Strain Measurements at 294 K for P(HEMA-*co*-EDMA) Hydrogels Prepared in the Presence of Different Concentrations of EDMA but at a Fixed Composition of HEMA and VP

xerogel	E, MN m^{-2}	ν_e, mol dm^{-3}	M_c, kg mol^{-1}	χ
HEMA70/VP30/EDMA0.25	1.00	0.144	8.8	0.740
HEMA70/VP30/EDMA0.50	1.01	0.143	8.9	0.741
HEMA70/VP30/EDMA0.75	1.22	0.171	7.4	0.745
HEMA70/VP30/EDMA1	1.75	0.245	5.2	0.746
HEMA70/VP30/EDMA2	1.77	0.245	5.2	0.746
HEMA70/VP30/EDMA4	2.99	0.411	3.1	0.792

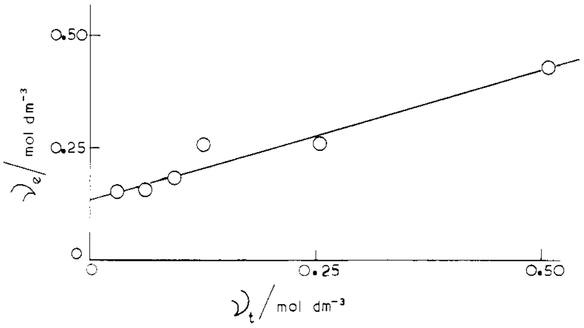

Figure 1. Dependence of measured effective cross-linking density on the theoretical cross-linking density for P(HEMA-*co*-VP-*co*-EDMA) hydrogels prepared in the presence of different concentrations of EDMA but a fixed composition of HEMA/VP = 70/30 (w/w).

values of $\alpha = 0.13$ mol dm^{-3} and $\beta = 0.55$ in the relationship:

$$\nu_e = \alpha + \beta\nu_t \tag{2}$$

The coefficient β is a measure of the efficiency of cross-linking, and the term α is the resultant of factors that induce a finite level of cross-linking in the absence of any added cross-linking agent. Values of β within the range $1 > \beta > 0$ are quite common for hydrogels. Thus $\beta = 0.82$ for P(HEMA-*co*-VP)[18] and for P(BA-*co*-VP-*co*-TPT) values of $\beta = 0.49$–0.60 according to the VP content have been reported.[3,4] The present value of $\alpha = 0.14$ mol dm^{-3} should correspond to the directly measured value of ν_e for the sample prepared in the absence of cross-linking agent, i.e. HEMA70/VP30, which is 0.063 mol dm^{-3} (see Table III). The difference between these two values must be considered significant. This factor, coupled with high sol fractions of these gels, prompted us to examine in a more detailed manner the compositional drift in the cross-linking copolymerization, with particular reference to the role of EDMA.

Composition at Different Conversions via the Q–e Scheme. Consider a system of n different monomers (M_1, M_2, ..., M_n). The instantaneous mole fraction F_1 of one of these (M_1) in the polymer (or copolymer, terpolymer, etc.) equals the rate of consumption of M_1 relative to the total rate of consumption of all n species.

$$F_1 = \frac{\mathrm{d}[M_1]/\mathrm{d}t}{\mathrm{d}(\sum_{i=1}^{n}[M_i])/\mathrm{d}t} \tag{3}$$

This can be transposed into the following more useful form in terms of mole fractions (f) of monomers in the feed

$$F_1 = 1/\sum_{i=1}^{n}(\mathrm{d}f_i/\mathrm{d}f_1) \tag{4}$$

In the Q–e scheme, Q and e are the general reactivity constant and general polarity constant, respectively. The Q and e values for a monomer are assumed to apply equally to its radical. The scheme can be adopted using the n-monomer substitution of Walling and Briggs[19] for $\sum_{i=1}^{n}\mathrm{d}[M_n]/\mathrm{d}[M_1]$ as discussed by Fordyce et al.[20] to yield

$$\frac{\sum_{i=1}^{n}\mathrm{d}[M_n]}{\mathrm{d}[M_1]} = \frac{A}{B} \tag{5}$$

where

$$A = [M_n]^2Q_n^2\exp(-e_n^2) + [M_1][M_2]Q_1Q_2\exp(-e_1e_n) + \ldots + [M_n][M_{n-1}]Q_nQ_{n-1}\exp(-e_ne_{n-1})$$

$$B = [M_1]^2Q_1^2\exp(-e_1^2) + [M_1][M_2]Q_1Q_2\exp(-e_1e_2) + \ldots + [M_1][M_n]Q_1Q_n\exp(-e_1e_n)$$

Expression 5 exists in a form that shows the individual steps in chain propagation: i.e., the summation of all the terms in the numerator and denominator represents the sum of all the possible propagation processes for addition of the given monomer to a growing chain. Equations 4 and 5 can now be put into the following form:

$$F_1 = \frac{f_1Q_1[\sum_{i=1}^{n}f_iQ_i\exp(-e_1e_i)]}{\sum_{\substack{i=1\\j=1}}^{n}[f_iQ_if_jQ_j\exp(-e_ie_j)]} \tag{6}$$

The denominator of eq 6 corresponds to the consumption of all monomers and hence will be the same for F_1, F_2, ..., or F_n. In contrast, the numerator will be different for F_1, F_2, ..., or F_n, because it defines the incorporation of specific monomers M_1, M_2, ..., or M_n into the polymer. At any stage of polymerization it holds also that

$$\sum_{i=1}^{n}F_i = 1 \tag{7}$$

If the Q_i and e_i values as well as the initial feed compositions f_i^0 are known for all the monomers involved, then the instantaneous polymer composition F_i can be obtained via eq 6 at the onset of polymerization. However, if instantaneous polymer compositions are required throughout the range of conversion, it is necessary to specify the interval of conversion during which the composition F_1 is attained. The smaller the interval taken, the more accurate will be the predicted drift in composition. Thus, on the assumption that 1% of the monomer originally present is converted to polymer of the predicted composition, an overall mass balance can be calculated:

$$\bar{F}_i = \sum_{x=1}^{100}F_i/x \tag{8}$$

In eq 8 $\bar{F}_i$ is the mole fraction of monomer i in the accumulated polymer (i.e. the average polymer composition) at the interval x of conversion, which is the percentage conversion in this case. After each interval of conversion, the composition of unreacted monomer feed f_i can be calculated from the following expression in which θ denotes the fractional conversion of all monomers:

$$f_i = (f_i^0 - \bar{F}_i\theta)/(1 - \theta) \tag{9}$$

This material balance yields new values for f_i after each interval of conversion. By repeating this sequence of procedures 100 times, for example, a graphical representation of the polymerization can be made. This me-

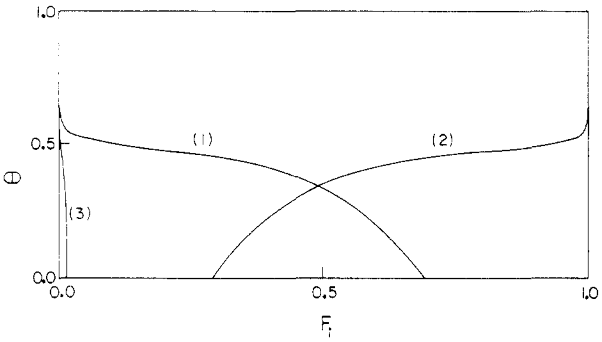

Figure 2. Theoretical plots of fractional conversion (θ) of monomers vs instantaneous mole fraction (F_i) of (1) HEMA, (2) VP, and (3) EDMA in the terpolymer of initial feed composition HEMA30/VP70/EDMA0.5.

thod, based on a procedure described by Seiner[21] and Friedman,[22] is applicable for any number (n) of monomers. Here a program was written in BASIC for use on an Amstrad 6128 microcomputer for $n = 3$. The output was in tabulated form. The Q and e values adopted for the three monomers were[23] the following: HEMA, $Q = 0.80$, $e = 0.20$; VP, $Q = 0.14$, $e = -1.14$; EDMA, $Q = 0.88$, $e = 0.24$.

A theoretical plot for the terpolymerization HEMA30/VP70/EDMA0.5 is shown in Figure 2 in which HEMA, VP, and EDMA represent monomers M_1, M_2, and M_3, respectively. The slopes of fractional conversion vs instantaneous mole fractions F_i in polymer become infinite on approach to $F_1 = 0$ and $F_3 = 0$ and on approach to $F_2 = 1$. The graphical format is very similar to that reported earlier for the two-component system.[7,8] The compositional drift in the HEMA/VP/EDMA terpolymerization is virtually identical with the previously shown[7] compositional drift in the HEMA/VP copolymerization. This is not unexpected, because the initial content of 0.5 wt % EDMA means that this monomer constitutes only a very small mole fraction of the feed ($f_3{}^0 \sim 0.003$), although for the calculations a value of $f_3{}^0 \sim 0.006$ was taken to account for the two vinyl groups per molecule of EDMA. However, the feature of especial significance is the compositional drift of EDMA. At $\theta \sim 0.50$–0.56 the EDMA and the HEMA in the feed are totally consumed, since $F_1 = F_3 = 0$ for these monomers at this conversion. Thereafter the polymer produced is almost pure P-VP. The net resultant polymer at $\theta = 1.00$ (i.e. at complete conversion) is predicted to consist of cross-linked P(HEMA-*co*-VP) [relatively rich in HEMA and EDMA with respect to their compositions in the initial feed] and a considerable quantity of P-VP, which may be lightly cross-linked by γ-irradiation and by reaction with pendant vinyl groups.

When the content of EDMA in the initial feed mixture is maintained approximately constant, but that of HEMA is increased (with a concomitant decrease in the content of VP), the situation alters. Parts a–d of Figure 3 relate to the four compositions HEMA15/VP85/EDMA0.5, HEMA30/VP70/EDMA0.5, HEMA45/VP55/EDMA0.5, and HEMA70/VP30/EDMA0.5, respectively. The curves show fractional conversion vs instantaneous mole fractions of HEMA and EDMA as F_1 and F_3 both approach zero, for the four HEMA/VP compositions. The regions of low F_1 and F_3 are considered, because they correspond to the direction of increasing conversion. These plots indicate the threshold conversions at which HEMA and EDMA are completely incorporated into the terpolymer and, hence equivalently, the quantity of P-VP generated in the later stages of polymerization. As the content of HEMA in the initial feed mixture ($f_1{}^0$) is increased, the conversion at which $F_1 \rightarrow 0$ for HEMA and $F_3 \rightarrow 0$ for EDMA becomes greater, thereby reducing the quantity of P-VP produced in the subsequent final stages of polymerization. The compositional drift of EDMA is also seen to decrease as the initial content of the feed increases [curve a through to curve d]. The overall consequences of this drift are expected to be (i) increasing water soluble fraction as the content of VP in the initial feed increases (at constant initial content of EDMA) and (ii) inhomogeneous cross-linking of the network especially at high content of VP in the initial feed.

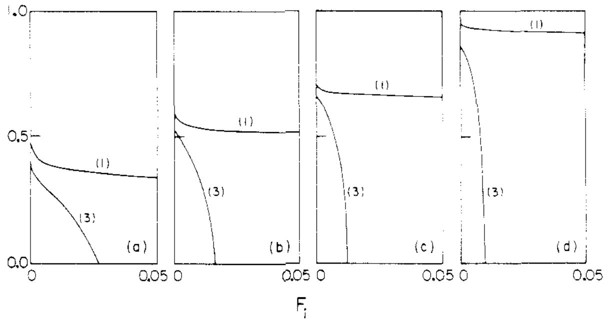

Figure 3. Theoretical plots of fractional conversion (θ) vs instantaneous mole fraction (F_i) of (1) HEMA and (3) EDMA over the interval $F_i = 0.00$–0.05 for the terpolymerizations of initial feed mixtures (a) HEMA15/VP85/EDMA0.5, (b) HEMA30/VP70/EDMA0.5, (c) HEMA45/VP55/EDMA0.5, and (d) HEMA70/VP30/EDMA0.5.

The present treatment provides an acceptable interpretation of some observations of other workers on these hydrogels and places them on a more quantitative basis. Thus, high sol fractions on swelling in water were noted by Franson and Peppas,[24] and Starodubstev et al.[25] reported that the cross-linking efficiency of EDMA decreased with increasing content of VP.

Finally we note that the analysis could have been made, in principle, in terms of the monomer reactivity ratios. For the HEMA/VP copolymerization the two values of these parameters are known, but for the terpolymerization there are four additional reactivity ratios required and these are not available. Consequently the Q–e scheme was used. When data are interpreted by means of this scheme, its semiquantitative nature should be borne in mind. Nonetheless, the behavior predicted by using this scheme seems to fit the observed results very well.

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Registry No. (HEMA)(VP) (copolymer), 29612-57-5; (EDMA)(HEMA)(VP) (copolymer), 36425-29-3; water, 7732-18-5.

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The Effect of Higher Order Interactions on Configurational Properties of Polymer Chains at the Θ State

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ABSTRACT: The configurational properties of polymer chains at the Θ state cannot be calculated exactly by two-parameter theories, because ternary (and higher order) interaction terms are still important. The size of the effect, which arises from the omission of these terms, was investigated. For this purpose, the characteristic ratios of simple chain models at the Θ state were evaluated by the RIS theory, which is based on two-parameter concepts, and by Monte Carlo methods at a state characterized by a vanishing second osmotic virial coefficient. The differences between the two results are considerable. On the other hand, the RIS theory has proved to be successful, when applied to more realistic models. The reasons for this apparent contradiction are discussed.

Introduction

When polymer molecules in dilute solution are treated by statistical mechanics, the complexity of the system is often reduced by considering the solvent as a continuum. The spatial configuration of a polymer molecule is thus governed by attractive and repulsive forces due to a potential of mean force, which depends on the temperature and the activity of the solvent. Through judicious selection of solvent and temperature, it is possible to obtain a state of the system at which attractive and repulsive forces are balanced and the solution behaves ideally in the thermodynamic sense. This means that the second osmotic virial coefficient vanishes. Flory defines this state as the Θ point of the polymer solution. It finds an exact parallel in the Boyle point of a real gas. Flory argues the following:[1–4] A state, where repulsion between a pair of chain units is exactly compensated by their mutual attraction, is equivalent to a state without any interaction involving pairs of units which are remote in the chain sequence. This means, a chain at the Θ point is equivalent to an unperturbed chain, the dimensions of which are influenced by short-range interferences solely.

The simplicity of Flory's concept allows model chains to be treated analytically in a straightforward manner, and many researchers have been inspired to develop corresponding formalisms. The results depend on the number of neighboring units considered to interact. The most refined model that has been treated up to now is the isomeric state model with interdependent rotation.[5–16] Flory devoted a comprehensive monograph to this topic.[4]

A quantitative description of the influence of intramolecular interactions on configurational and thermodynamic properties was first given by the two-parameter theory, the perturbation version of which can be sketched in its essential parts by

$$\langle h_n^2\rangle/\langle h_n^2\rangle_0 = 1 + \beta_2 f(\beta_2,n) \qquad (1)$$

and

$$A_2(n) = n^2\beta_2 g(\beta_2,n) \qquad (2)$$

$\langle h_n^2\rangle$ is the mean-square end-to-end distance of a chain with n bonds, β_2 is the binary cluster integral,

$$\beta_2 = \int\left\{1 - \exp\left[-\frac{w(\mathbf{r})}{kT}\right]\right\} \mathrm{d}\mathbf{r}$$

and A_2 is the second osmotic virial coefficient. The subscript 0 refers to a reference chain, generally a model chain with short interferences only, which resembles the essential features of the perturbed chain to be studied. If $A_2 = 0$, it follows from eq 2 that $\beta_2 = 0$ and therefore (eq 1) $\langle h^2\rangle_\Theta = \langle h^2\rangle_0$. This is in accordance with Flory's statements. The perturbation development given above, however, is incomplete. It does not include cluster integrals of higher order. (Flory[17] considered higher interaction terms in a theory on A_2, but he supposed their contribution to be small; so he neglected them in later work.) In most cases these terms are small compared with the binary interaction terms, and they can, therefore, be neglected. In the vicinity of the Θ temperature, however, the binary interaction terms assume values of the same order of magnitude as the higher interaction terms, so that the latter have also be taken into account.[18] The supplemented equations thus read

$$\langle h_n^2\rangle/\langle h_n^2\rangle_0 = 1 + \beta_2 f_2(\beta_2,n) + \beta_3 f_3(\beta_2,\beta_3,n) + \ldots$$

and

$$A_2(n) = \beta_2 g_2(\beta_2,n) + \beta_3 g_3(\beta_2,\beta_3,n) + \ldots$$

with the tertiary cluster integral

$$\beta_3 = \int \chi_{ij}\chi_{jk}\chi_{ik}\,\mathrm{d}\mathbf{r}_{ij}\,\mathrm{d}\mathbf{r}_{jk}$$

$$\chi_{\alpha\beta} = 1 - \exp\left[-\frac{w(\mathbf{r}_{\alpha\beta})}{kT}\right]$$

β_2 and β_3 do not vanish simultaneously at the same tem-

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