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Characteristics of copolymerizations involving dimethylacrylamide and swelling behaviour of the copolymers in water

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The free radical copolymerizations of dimethylacrylamide (DMA) with ethylene dimethacrylate (EDMA) and of DMA with methyl methacrylate (MMA) have been conducted over a wide range of conversion. Compositions of resultant crosslinked poly(DMA-*co*-EDMA) and of linear poly(DMA-*co*-MMA) were determined by nitrogen analysis and *FT*i.r., respectively. Appropriate modern procedures applied to the data yielded reactivity ratios of $r_{\mathrm{DMA}} = 0.51 \pm 0.15$, $r_{\mathrm{MMA}} = 2.07 \pm 0.19$ and $r_{\mathrm{DMA}} = 0.9 \pm 0.2$, $r_{\mathrm{EDMA}} = 1.8 \pm 0.6$, the latter pair being obtained neglecting possible reactivity of pendant double bonds. γ-Irradiation of DMA/MMA mixtures both in the absence and presence of EDMA yielded highly swellable crosslinked xerogels. The equilibrium water content of the hydrogels increased with increase of DMA in copolymer and with decreasing content of EDMA. Over the range of swelling temperature examined, 280–338 K, the swelling was found to be exothermic. At comparable molar compositions, these materials exhibited higher water contents than the corresponding hydrogels containing *N*-vinyl-2-pyrrolidone in place of DMA. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(dimethylacrylamide-*co*-methyl methacrylate); poly(dimethyl acrylamide-*co*-ethylene dimethacrylate); reactivity ratios; hydrogel; exothermic swelling)

INTRODUCTION

Of the methods available for producing hydrogels, one of the most convenient is to swell to equilibrium in water the dry product (xerogel) of polymerization or copolymerization in the presence of a crosslinker. The overall swelling capacity is dictated mainly by the nature of the monomers and composition of copolymer; the nature and concentration of crosslinker occupy an important but lesser role in this respect. When the co-monomers are miscible, the xerogel is normally a clear solid; in other circumstances an inert compatibilizing diluent[1] (e.g. water) must be included in the feed mixture with the result that the product is a partially swollen xerogel.

Apart from polyelectrolyte systems, most feed mixtures studied comprise appropriate combinations of a hydrophilic and a hydrophobic monomer. Within the former category, the liquid monomers *N*-vinyl-2-pyrrolidone (VP) and 2-hydroxyethylmethacrylate (HEMA) have received intensive investigation. The swelling characteristics of hydrogels based on crosslinked copolymers containing VP with a variety of co-monomers have been compared and collated elsewhere[2]. With the exception of one copolymeric system displaying synergism in swelling behaviour[3] and crosslinked poly(HEMA-*co*-VP) itself[4], the swelling capacity of copolymeric xerogels containing HEMA are restricted by the only moderate swellability of polyHEMA. No such restriction applies with VP as a co-monomer, but the small reactivity ratio of VP in its free radical copolymerization gives rise to considerable compositional heterogeneity and, especially important for practical applications, a significant sol fraction of polyVP (or copolymer of very high VP content) in material prepared to high conversion[5].

In this work we consider a viable alternative to VP as a co-monomer. VP is a lactam bearing a formal analogy with the simple amide, acrylamide (AM). However, although AM has been employed extensively to prepare linear polyAM by inverse emulsion polymerization[6–9] and to prepare copolymers with ionic co-monomers for water treatment[10], it is less suitable for the present purpose due to the fact that it is a solid and is immiscible with common neutral co-monomers.

However, the liquid monomer *N*,*N*-dimethylacrylamide (DMA) is miscible with several co-monomers and, despite the replacement of the two hydrogen atoms in AM by methyl groups, the hydrophilicity is known to be retained. Thus linear polyDMA is water soluble and no upper or lower critical solution temperatures in aqueous polyDMA have been detected within the interval 273–473 K[11].

The present work focuses on two main objectives (1) the swelling behaviour of chemically crosslinked copolymers containing DMA with the common hydrophobic co-monomer methyl methacrylate (MMA) and (2)

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*To whom correspondence should be addressed determination of the relevant reactivity ratios in the crosslinking copolymerization whereby the xerogels are produced, since these parameters are useful in describing the form of compositional heterogeneity at various stages of conversion and also for predicting the occurrence or extent of sol fraction.

EXPERIMENTAL

Materials

MMA (Fisons) was dried with $MgSO_4$ and then redistilled at 373–374 K. DMA (Aldrich) was distilled under reduced pressure (323–324 K/3–4 mm Hg) prior to use. EDMA (Aldrich) was vacuum distilled at 349–350 K/0.3 mm Hg. α,α'-Azo-isobutyronitrile (AIBN, Fluka) was recrystallized from ethanol/toluene. Chloroform was shaken with dilute H_2SO_4, washed thoroughly with water, and dried with $CaCl_2$ before filtering and distilling. 1,4-Dioxane (BDH) was dried with $MgSO_4$ overnight and distilled at 373–374 K. Methanol, ethanol, toluene, petroleum ether (333–353 K) and n-heptane (Fisons) were used as received, and deionized water was used for swelling.

Copolymerization and analysis of copolymer composition

DMA–EDMA system. The copolymerization in bulk of DMA with EDMA was carried out at 333 K by AIBN initiation after degassing for 10 min with N_2. Reactions were conducted for different times in order to obtain various stages of fractional conversions on a weight basis θ. After a particular time of reaction, 6–7 times by volume of petroleum ether was added and the precipitated copolymer was washed thoroughly with the petroleum ether before drying to constant weight.

A Kjeltec Auto 1030 Analyzer was used to measure the nitrogen content of the homopolymer of DMA and the copolymers. A small correction factor, based on the theoretical %N for pure polyDMA relative to the measured %N of polyDMA was applied.

DMA–MMA system. Copolymerizations were conducted as above with the exceptions that (i) dioxane was included as solvent, (ii) the temperature was 343 K, and (iii) copolymer was isolated by adding solution to excess of precipitant and purified by redissolving in chloroform, and reprecipitation.

The copolymer compositions were determined by *FT*i.r. analysis[12], spectra of solutions in chloroform of the copolymers, homopolymers and homopolymer blends being recorded on a PE 1710 *FT*i.r. spectrometer. Measurements were made under conditions of eight scans, 2 cm^{-1} resolution and interleaved mode. The same liquid cell was used for all the measurements. The concentration of all solutions was 1.8 %w/v.

Copolymers prepared for swelling

Mixtures of monomer were made up gravimetrically in previously siliconized[13] glass tubes and then subjected to γ-irradiation from the 333 T Bq ^{60}Co source at Salford University to a total dose of 20 k Gy at a dose rate of 10 Gy h^{-1}. After their removal from the tubes the resultant solid rods of xerogel were oven cured for 24 h at 378 K. The small weight loss on oven curing indicated that the conversion of monomers was always in excess of 99%. The xerogels were finally lathe cut into discs (diameter 10 mm, thickness 1 mm).

Table 1 Copolymerization data for the DMA–EDMA system

Copolymer	f_1^0	wt%N	F_1	θ
DE-1	0.331	2.75	0.325	0.966
DE-2	0.183	1.39	0.179	0.953
DE-3	0.568	5.73	0.577	0.943
DE-4	0.667	7.33	0.683	0.959
DE-5	0.748	8.89	0.772	0.983
DE-6	0.832	9.76	0.817	0.368
DE-7	0.474	4.49	0.482	0.981
DE-8	0.951	12.49	0.938	0.230
DE-9	0.665	5.56	0.565	0.183
DE-10	0.748	7.92	0.718	0.302
DE-11	0.559	3.36	0.384	0.113
DE-12	0.450	4.15	0.454	0.203
DE-13	0.332	1.65	0.209	0.078
DE-14	0.191	0.64	0.086	0.154
DE-15	0.860	10.83	0.868	0.289
DE-16	0.386	3.55	0.401	0.301
DE-17	0.456	2.42	0.292	0.104

Swelling

The discs of xerogel were Soxhlet extracted with water for 48 h to remove any sol fraction. The resultant dried discs were then swollen to equilibrium at a series of constant temperatures.

The equilibrium water contents W_1 were obtained as follows:

$$W_1 = 100(m - m_2)/m$$

where m_2 and m denote, respectively, the weights of dry xerogel and swollen gel, the latter being obtained after lightly surface drying the swollen gel.

RESULTS AND DISCUSSION

Reactivity ratios

DMA–EDMA system. The mole fractions f_1^0 of DMA in the initial feed mixture, the conversions θ, the nitrogen contents of copolymers and the mole fractions F_1 of DMA units in the copolymers are listed in *Table 1*. These data are given in full for the benefit of others wishing to treat them by procedures other than those adopted here. In principle this copolymerization should be considered really as a terpolymerization due to the two double bonds in EDMA. Thus there is the possibility of pendant double bonds participating in cyclization and other reactions. Here, however, we neglect this complicating factor and invoke the normal terminal model according to the convention that the divinyl monomer can be treated in the same way as a normal vinyl one. We have adopted this procedure previously in determining the reactivity ratios in the system EDMA–MMA[14]. Reference should be made to the relevant report in which details and justification for the approach are amplified. It should be noted that, although approximate in principle, this procedure afforded reactivity ratios which afforded theoretical composition–conversion curves on which the experimental data fell extremely well[14]. As pointed out by Dušek and Spěváěek[15], in spite of the strong cyclization and deviation in crosslinking copolymerization

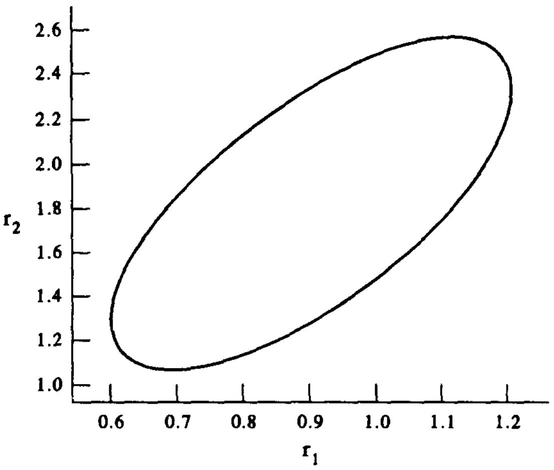

Figure 1 95% joint confidence region of the reactivity ratios of the DMA–EDMA system from the M–H method

Table 2 Copolymerization data for the DMA–MMA system

Copolymer	f_1^0	F_1	θ
D-M1	0.062	0.030	0.200
D-M2	0.100	0.050	0.120
D-M3	0.183	0.096	0.285
D-M4	0.218	0.143	0.125
D-M5	0.255	0.152	0.104
D-M6	0.343	0.090	0.281
D-M7	0.348	0.232	0.286
D-M8	0.445	0.295	0.096
D-M9	0.456	0.302	0.121
D-M10	0.482	0.332	0.092
D-M11	0.497	0.345	0.108
D-M12	0.518	0.372	0.350
D-M13	0.636	0.474	0.141
D-M14	0.638	0.512	0.213
D-M15	0.738	0.587	0.122
D-M16	0.790	0.147	0.094
D-M17	0.795	0.680	0.543

from the usual view, the copolymerization parameters determined with neglection of cyclization need not be too distorted..

With regard to manipulation of the present data (*Table 1*), three modern approaches have been considered, viz. the Kelen–Tüdös (K–T) method[16], the extended Kelen–Tüdös (Ex K–T) method[17] and the iterative procedure (M–H) due to Mao and Huglin[18]. The K–T method would involve the use of only a very small number of the available data, since the procedure is restricted to those for low conversion. The value of the conversion θ is used in the Ex K–T method, but here again not all of the data can be used, since the method is known to be reliable only for $\theta \ngtr$ *ca.* 0.4–0.5. In contrast, the M–H method which also involves the values of θ in the calculation, is applicable to very high values of θ. Use of the M–H method yielded:

$$r_1(\text{DMA}) = 0.9 \pm 0.2 \text{ and}$$

$$r_2(\text{EDMA}) = 1.8 \pm 0.6$$

The 95% joint confidence region is shown in *Figure 1*.

DMA–MMA system. The i.r. spectra of PDMA and PMMA exhibit strong bands at 1729 and 1639 cm^{-1}, respectively, which are due to the carbonyl in ester groups of MMA and the carbonyl in N-substituted amide groups of DMA, respectively. The location and the shape of the two peaks of PDMA/PMMA blends are very similar to those for a copolymer of DMA and MMA (*Figure 2*). Hence the i.r. method[12] is a suitable procedure for determining the compositions of the copolymers. Chloroform was chosen as solvent not only because it is a good solvent for both homopolymers and copolymers, but also because it has no absorption in the region of 1600–1750 cm^{-1}. Calibration was affected with solutions of blends of PDMA and PMMA containing accurately known weight fractions, W_1 of PDMA. Seventeen different values of W_1 covering the whole range of composition were used and, after correction for the base line, the absorbances (A) were measured. The absorbance ratio $A_{1639}/(A_{1639} + A_{1729})$ as a function of W_1 was used as calibration, the curve being fitted to the polynomial ($r^2 = 0.9998$)

$$\frac{A_{1639}}{A_{1639} + A_{1729}} = 6.5 \times 10^{-4} + 1.739W_1 - 1.673W_1^2 + 1.665W_1^3 - 0.782W_1^4 + 0.0508W_1^5 \qquad (1)$$

For 17 copolymers produced from feed mixtures of different initial mole fractions f_0^1 of DMA, the cumulative copolymer compositions W_1 were obtained via equation (1) from the measured absorbance ratios. The values of W_1 were converted to mole fractions F_1 of DMA in copolymer. These with the relevant values of f_1^0 and measured conversions θ are listed in *Table 2*. Because the data are not consistently for low conversion, only the Ex K–T and M–H procedures were used to derive r_1(DMA), r_2(MMA) and the relative error parameter $\delta^{\square}$ defined as follows:

$$\delta^{\square} = \left| \frac{\Delta r_1 \Delta r_2}{r_1 r_2} \right| \qquad (2)$$

The results are:

Ex K–T, $r_1 = 0.49 \pm 0.15$, $r_2 = 2.04 \pm 0.22$, $\delta^{\square} = 0.0334$
M–H, $r_1 = 0.51 \pm 0.15$, $r_2 = 2.07 \pm 0.19$, $\delta^{\square} = 0.0263$

Although the M–H procedure affords a smaller value of $\delta^{\square}$ than that yielded by Ex K–T procedure, the reactivity ratios from both methods are in reasonably close accord. From the fact that the values of $\delta^{\square}$ are considerably smaller than 0.1 it may be concluded that this copolymerization belongs to Class 1 defined by Tüdös *et al.*[19], i.e. a strictly linear system describable by the terminal model, thereby allowing accurate reactivity ratios to be obtained. Hence use of the penultimate model is unnecessary.

The present findings may be compared with literature values for this system listed in *Table 3*. Although the small and large values of r_1 and r_2, respectively, in ref. 24 may be a consequence of the use of charge transfer initiation by Srinivasulu *et al.*, a similar direction of departure from our values is evident in ref. 22, where normal free radical initiation was used. The closest accord with the present findings is seen in the first two entries in *Table 3*, which is surprising, since rather outdated and somewhat suspect methods were used to derive the reactivity ratios. Despite these methods, it is perhaps noteworthy that their use applied to very low conversion data yields reactivity ratios which are similar in value to those derived here by more sophisticated means from data for medium conversion data.

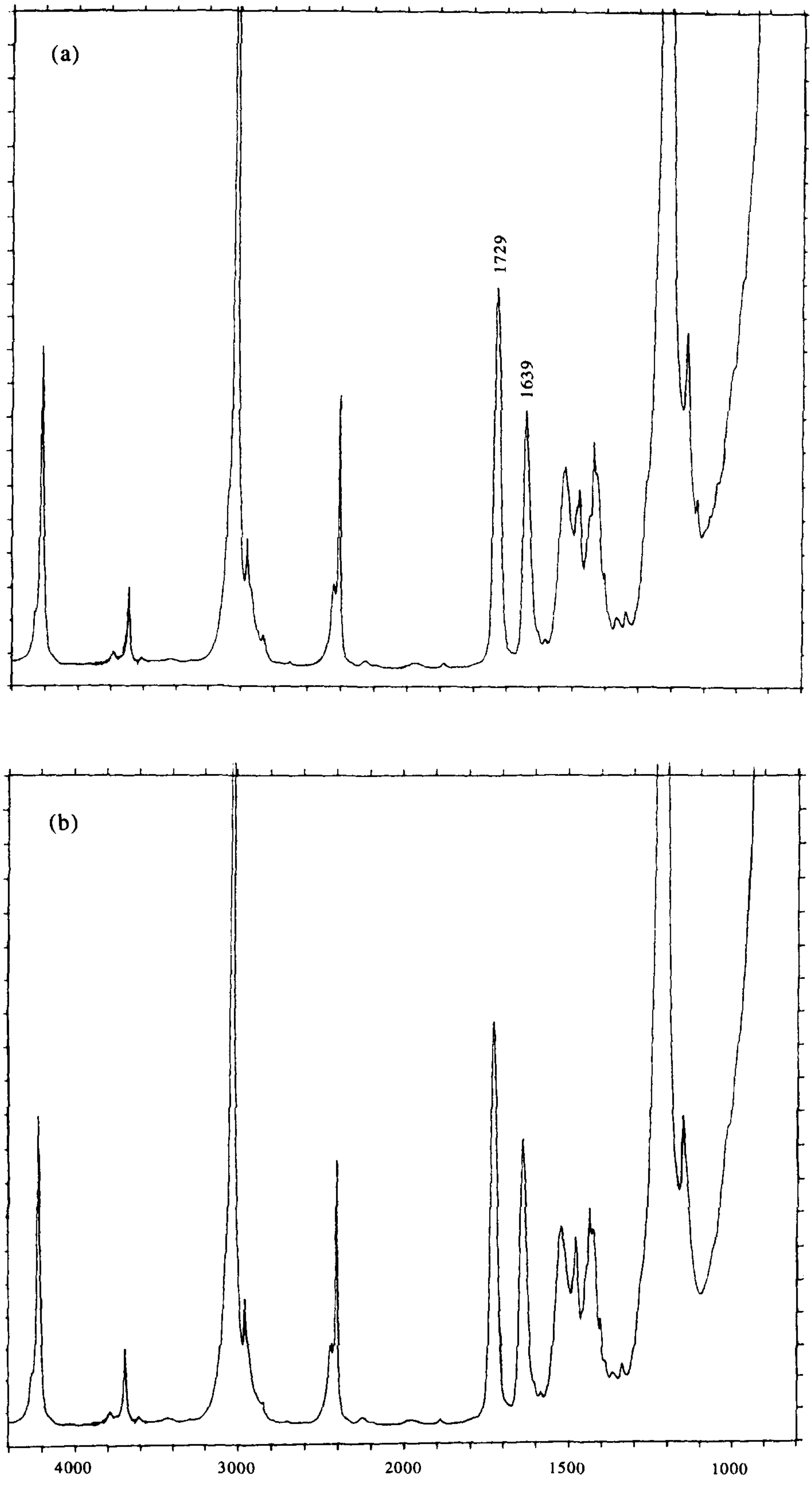

Figure 2 *FT*i.r. spectra of (a) PDMA/PMMA (30/70 wt%) blend and (b) poly(DMA-*co*-MMA) (30/70 wt%) in chloroform

HYDROGELS

Effect of composition and crosslinking on swelling

Initially copolymers were prepared in the absence of crosslinker (EDMA). After Soxhlet extraction in water the sol fractions were calculated to be fairly small, decreasing in the sequence 13.8, 7.9, 5.0, 2.0 and 0 wt% as the wt% DMA in the copolymer decreases in the order 80, 65, 50, 35 and 18 wt%. Since $r_{DMA} < r_{MMA}$, MMA is consumed more readily initially and incorporation of its more hydrophilic co-monomer occurs preferentially at large θ. Hence the higher the initial content of DMA in the feed the greater the tendency for copolymer produced in the later stages to have a high DMA content and be

Table 3 Comparison of reported reactivity ratios for the copolymerization[a] of DMA (M_1) and MMA (M_2)

r_1	r_2	Solvent	T(K)	θ	Method	Ref.
0.45 ± 0.08	1.8 ± 0.18	toluene	323	< 0.05	intersection	20
0.51 ± 0.07	2.04 ± 0.11	dioxane	343	< 0.10	F–R[b]	21
0.42 ± 0.10	2.30 ± 0.24	ethanol	343	< 0.10	F–R	21
0.218 ± 0.007	2.650 ± 0.100	dioxane	338	< 0.10	F–R	22[c]
0.58	2.21	ethanol	343	< 0.10	NLLS[d]	23[e]
0.24 ± 0.01	2.86 ± 0.02	DMSO	333	< 0.10	F–R	24[f]
0.23 ± 0.01	2.86 ± 0.02	DMSO	333	< 0.10	K–T	24[d]

[a] All copolymer compositions were determined by nitrogen analysis
[b] Fineman–Ross plot
[c] Half monomer was added dropwise to another half monomer in the reaction flask
[d] Non linear least squares
[e] Using the experimental data of ref. 20
[f] Charge transfer initiated copolymerization

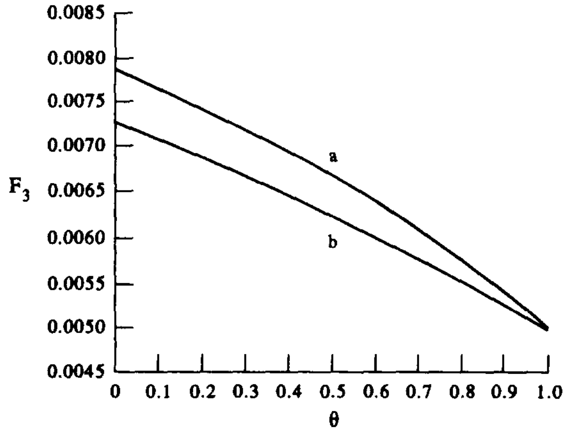

Figure 3 Cumulative mole fraction of EDMA (F_3) at various stages of conversion (θ) for copolymerization of DMA with MMA in the presence of 1 wt% EDMA for initial concentrations of DMA of (a) 35 wt% and (b) 80 wt%

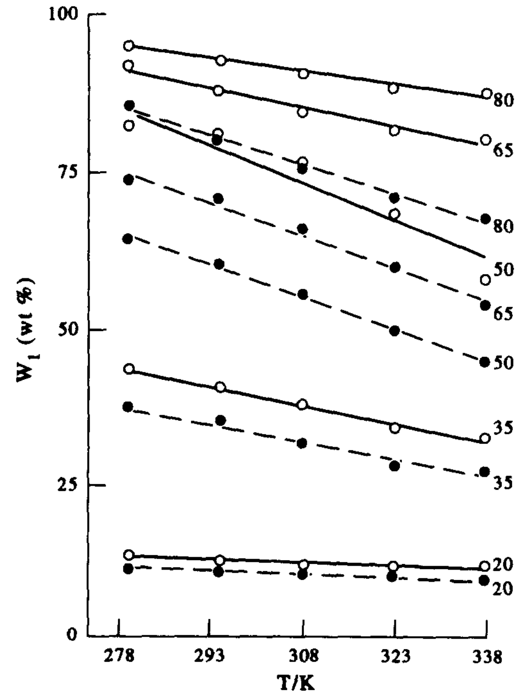

Figure 4 Variation of water contents with temperatures for hydrogels based on poly(DMA-*co*-MMA) xerogels. Numbers indicate wt% DMA in xerogel. Open circles (○) relate to copolymers prepared in the absence of EDMA and filled circles (●) to those prepared in presence of 1 wt% EDMA

water soluble. This general characteristic is accentuated even further in the system VP/MMA which has a much greater disparity between the very small r_{VP} and the very large r_{MMA}[25] and much larger sol fractions are obtained[5]. When EDMA is included in the copolymerization at a concentration of 1 wt%, the sol fractions in the same order of decreasing content of DMA indicated above are 13.1, 7.8, 0, 0.6 and 0 wt%. Hence the effect of EDMA in reducing the sol fraction is only slight for systems of high DMA content, but for samples of low content of DMA the smallish sol fractions are reduced effectively to zero. This observation may be explained, at least in part, by correlating incorporation of EDMA with crosslinking and resultant reduction in sol fraction. To illustrate this we have calculated the cumulative mole fraction F_3 of EDMA in copolymer at all stages of conversion. *Figure 3* shows that the values of F_3 for the system of 35 wt% DMA are consistently higher than those having 80 wt% DMA, even though the initial content of EDMA is 1 wt% for both cases.

The effect of increasing the concentration even further has been examined for only one system, viz. the copolymers containing 50 wt% DMA. As already noted, the 5% sol fraction obtained in the absence of EDMA is reduced to 0% when 1 wt% EDMA is incorporated. As expected, the sol fraction remains zero at 2, 3 and 5% EDMA contents. Hence, although it is not established if $< 1\%$ is sufficient, the main effect in using high concentrations of crosslinker is to alter the level of swelling (see further) rather than the sol fraction. In view of previous comments and *Figure 3*, it is important to realize that the effect of high (2–5 wt%) EDMA contents may well not hold for systems of $> 50\%$ DMA.

With regard to swellability of the copolymers, we shall consider first the values of W_1 at 295 K (similar trends hold at other temperatures dealt with in the next section). The most significant finding is that the Soxhlet extracted materials prepared in the absence of EDMA all exhibited high swelling capacity without physical disintegration. For the five samples of DMA content decreasing from 80 to 20% the values of W_1 decreased from 92.5 to 11.0%. It may be reasonably surmised, therefore, that crosslinking was induced by the γ-irradiation. For samples produced in the presence of 1 wt% EDMA the same sequence of decrease in W_1 was observed, but all values were smaller than the corresponding ones for copolymers prepared in the absence of EDMA, e.g. sample containing 80 wt% DMA and 1% EDMA yielded $W_1 = 80.6\%$ (instead of 92.5%).

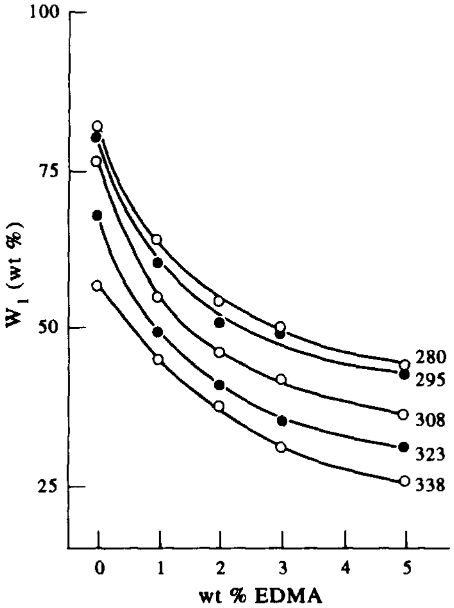

Figure 5 Variation of water content of hydrogel with concentration of EDMA in xerogels for poly(DMA-*co*-MMA) containing 50 wt% DMA. Numbers indicate the swelling temperatures (K)

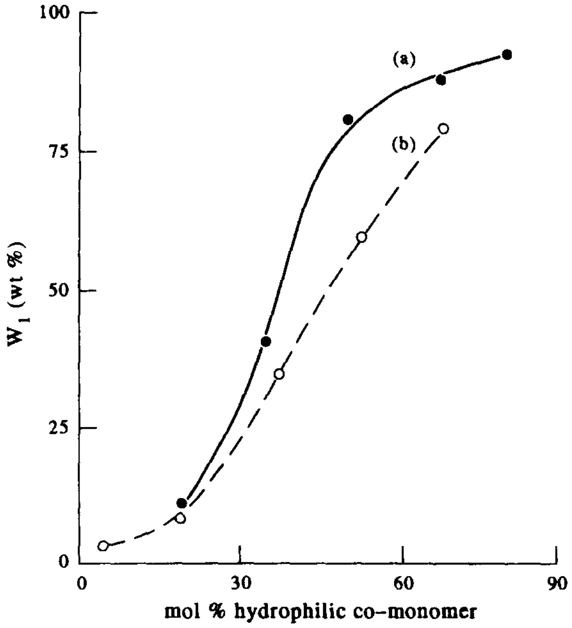

Figure 6 Dependence of water content of hydrogels at 294 K on composition of xerogels for copolymers based on MMA with the hydrophilic co-monomers (a) DMA and (b) VP[5]

Effect of temperature on swelling

The variation of the equilibrium water content with the temperature T is illustrated in *Figure 4* for the copolymers of five different compositions over the interval 280–338 K. The decrease in W_1 with decreasing content of DMA referred to previously with respect to 295 K, applies equally to each of the other temperatures. Within the temperature range covered, the fall in W_1 with increasing T is linear. For the samples of lowest DMA content the fractional change in W_1 relative to the value at 280 K is *ca* −0.002 per degree. The corresponding quantity for the sample of highest DMA has a lower value of *ca* −0.001 per degree. The inclusion of 1 wt% EDMA in the copolymer decreases W_1 at corresponding copolymer compositions and temperature, but the decrease in W_1 with T is of a very similar form to that exhibited by samples not containing EDMA.

Swelling measurements for copolymers having a fixed content (50 wt%) of DMA but various contents of EDMA were conducted at each of the same five temperatures. The plots of W_1 vs T for each sample are not reproduced here, since they are of the same general form as those in *Figure 4* (which actually contains two of them, viz. for 0 and 1% EDMA). Instead, the variation of W_1, with EDMA content is shown for each temperature in *Figure 5*. The dependence is not linear and it is evident that the reduction in swelling is most marked on introduction of only a small quantity of crosslinker.

Finally it is of interest to make some comparisons of these hydrogels with the corresponding ones containing VP in place of DMA. First, both types of copolymer are able to participate in hydrogen bonding with water and the present linear decrease in W_1 with T is in general accord with the (non-linear) decrease in W_1 reported for both chemically[5] and physically[26] crosslinked poly(VP-*co*-MMA) in water. Secondly, however, a difference in hydrophilicity is evident between the two systems. Thus to allow for the difference in molecular masses of DMA and VP units, we have calculated the molar composition of hydrophilic unit (VP or DMA) in the xerogels. *Figure 6* illustrates the variation of W_1 with composition. It is seen that at comparable mol % hydrophilic unit, the values of W_1 tend to be greater when DMA is the hydrophilic co-monomer than when the co-monomer is VP[5]. *Figure 6* relates to xerogels prepared by γ-irradiation in the absence of EDMA. Findings of a similar general form (not illustrated here) hold for swelling of corresponding copolymers prepared in the presence of 1 wt% EDMA.

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