Effects of poly(vinyl acetate) and poly(methyl methacrylate) low-profile additives on the curing of unsaturated polyester resins: rheokinetics and morphological changes up to gelation

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The effects of two low-profile additives (LPA), namely poly(vinyl acetate) and poly(methyl methacrylate), on the rheokinetics and morphological changes up to gelation in the cure of unsaturated polyester (UP) resins at 110°C were investigated by using a Haake viscometer, a differential scanning calorimeter, a Fourier-transform infra-red spectrometer and a scanning electron microscope. Adding LPA to the neat UP resins could increase the gel time and the gel conversion to differing extents, depending on the types of LPA added. The experimental results were explained by a microgel-based gelation mechanism on the basis of the integrated rheology–reaction kinetics–morphology results and by ternary static phase characteristics for styrene/UP/LPA systems at 25°C.

(Keywords: unsaturated polyester resins; low-profile additives; rheokinetics)

INTRODUCTION

In the reactive processing of unsaturated polyester (UP) moulding compounds, gelation characteristics are one of the most important factors in determining the processing conditions. For example, fast gelation at too high a curing temperature should be avoided, otherwise incomplete mould filling or poor surface finish of moulded parts could result.

Many researchers have studied the rheokinetics of neat UP resins[1–6]. The gelation time was determined either by measuring steady shearing flow properties[1–5], which characterized the rheological behaviour of materials in the liquid state, or by the crossover of the storage modulus G' and the loss modulus G'' in the measurement of oscillatory shearing flow properties[6], which characterized the rheological behaviour of materials in both the rubbery and glassy states. In general, the gel time determined by the former method was 30–40% greater than the time when $G'=G''$ was measured[6], which may not be the actual gel point. For the overall conversion of UP resins at the gel point, it was mostly obtained indirectly by comparing the conversion vs. time profile measured by differential scanning calorimetry (d.s.c.) or Fourier-transform infra-red spectrometry (*FT*i.r.) with the rheological measurement on the same cure time basis[1,5,6], which gave gel conversion values of 1–6%. A gel conversion of 20% was reported[2], which was determined by direct measurement of the conversion for partially cured samples before the gel point using infra-red spectrometry. In theoretical work, Yang and Suspene[3] and Suspene *et al.*[4] have recently proposed a gelation model concerning the formation of microgels for the prediction of viscosity rise during curing before gelation. The model described the gelation mechanism in four stages, namely, induction, microgel formation, transition stage and macrogelation. They claimed that, in the prediction of gel time, the conversion of UP resins during curing prior to gelation (i.e. reaction kinetics) could be excluded from the gelation model they proposed. Gelation was simply assumed to occur at a critical free-radical concentration, which could be determined by the concentrations of initiator and accelerator and the curing temperature for a specific resin system[3]. As the resin structure and the initial molar ratio of styrene to polyester C=C bonds varied, the critical free-radical concentration also changed, which could be interpreted by system miscibility indicated by Flory interaction parameter[4], χ.

For UP resin with low-profile additive (LPA), Lee and Han[7] measured the gel time by conducting both steady and oscillatory shearing flow measurements at 110°C. The gel times by the former measurement were more than twice as large as those by the latter measurement. They also found that the gel times were shorter for the UP resin with LPAs containing unsaturated C=C double bonds than those without unsaturated double bonds (e.g. poly(vinyl acetate), PVAc). No gel conversion was measured. Hsu and Lee[8] and Hsu *et al.*[9] found that adding LPA to the neat UP resin could not only delay the time to reach $G'=G''$ but also raise the conversion at that point. The conversion at the liquid–solid transition as

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indicated by the point $G' = G''$ was less than 1% at 75–85°C and ranged from 1 to 4% at 35–50°C. By judging from a large measured gel fraction (near 30%) of the PVAc-containing sample at the $G' = G''$ point, they suggested[9] that, at the gel point, chemical crosslinking would be more favourable in reactions of UP resins without LPA, while physical crosslinking, such as phase formation and inversion, would play an important role in reactions with LPA. By adapting the same concept as that of Yang and Suspene[3] and Yang and Algare[10], Muzumdar and Lee[11] have proposed a gelation model, which assumed that gelation occurred at a critical radical concentration, for prediction of the gel time in the cure of UP resins containing LPA.

For vinyl ester resins with LPA, Hong and Chung[12] reported that adding LPA to the vinyl ester resins could also prolong the gel time, but the gel conversion was essentially unchanged. By comparing the reaction conversion data measured by d.s.c. and the shearing flow viscosity data on the same basis of cure time, the gel conversion at a level of 62–64% was obtained at 90°C. They also found that vinyl ester resin with a compatible LPA, such as PVAc, showed faster gelation than that with an incompatible LPA, such as poly(methyl methacrylate) (PMMA).

In the past, the reaction kinetics in the cure of UP resins with LPA has been investigated solely by using d.s.c. Also, almost all the gel conversion data have been obtained indirectly by comparison of the rheological data and the reaction kinetics data on the same cure time basis, which may not reflect the true gel conversion. In our previous work[13], the characterization of detailed reaction kinetics by *FT*i.r. in the cure of UP resins with LPA has been dealt with for the first time in the open literature. In this work, the effects of two low-profile additives (LPA), poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA), on the rheokinetics and morphological changes up to gelation in the cure of UP resins at 110°C were studied by an integrated rheology–reaction kinetics–morphology measurement using a Haake viscometer, d.s.c., *FT*i.r. and SEM. The conversions of styrene, polyester C=C bonds and overall C=C bonds were measured directly for partially cured samples prior to gelation by using d.s.c. and *FT*i.r. The gel conversion thus obtained was compared with that by the indirect comparison of rheological and overall conversion measurements on the same cure time basis. Based on the experimental results, the effects of LPA on gel time, gel conversion, associated morphological changes prior to gelation and gelation mechanism are discussed.

EXPERIMENTAL

Materials

The unsaturated polyester resin and LPAs used were the same as those in the previous paper[13]. The UP resin contained isophthalic acid, fumaric acid and propylene glycol with a molar ratio of 1:1.70:2.73 by ^{1}H n.m.r. analysis. The acid value and the hydroxyl number of the resin were found to be 24.5 and 27.8, respectively, by end-group titration, which gives a number-average molar mass of 2140 g mol^{-1}. On average, the calculated number of C=C bonds in each polyester molecule was 7.72. The molar ratio of styrene to polyester C=C bonds in the resin was adjusted to be $MR = 2/1$ in the preparation of the sample solutions. Sample solutions with $MR = 1/1$, 3/1 and 6/1 were also prepared.

In this study, the two LPAs employed were poly(vinyl acetate) (PVAc; LP40A, Union Carbide) and poly(methyl methacrylate) (PMMA). The number-average molar masses for PVAc and PMMA were measured to be 42 000 and 34 000 g mol^{-1}, respectively, by vapour pressure osmometry (v.p.o.). For the sample solution with LPA, 10% by weight of LPA was added, while the molar ratio of styrene to polyester C=C bonds was still adjusted to be $MR = 1/1$, 2/1, 3/1 or 6/1. The reaction was initiated by 1% by weight of t-butyl perbenzoate (TBPB) at 110°C. All the materials were employed as received without further purification.

Instrumentation and procedure

For the rheological measurement during the curing, a Haake viscometer model RV20/M10 was used to measure the viscosity change prior to the gelation. Some sample solution (2–3 g) was placed inside a Couette SVII type of measuring unit, and the viscosity vs. time profile was then measured under atmospheric pressure at 110°C. The gelation time may be determined when the sample viscosity started to rise sharply. By comparing the viscosity measurement data with the reaction conversion data measured by d.s.c. or *FT*i.r. on the basis of the same cure time, the gel conversion was obtained indirectly. In addition, the gel conversion of the sample solution was measured directly as follows. First, 2 g of sample solution was sealed in a 50 × 6 mm thin aluminium disc mould. Several such moulds were then placed simultaneously into a thermostated silicone oil bath at 110°C. By referring to the viscosity vs. time profile measured by the Haake viscometer, the reaction of resin cured in the mould was stopped at each preset time by removing one of the disc moulds from the oil bath and quenching it in liquid nitrogen for 5 min to prevent any further reaction. Four to six such partially cured samples at various degrees of cure were thus obtained. By a Haake viscometer with a cone-and-plate measuring unit (PK1, 1°), the viscosity of partially cured samples at room temperature was measured.

For the overall conversion of the partially cured samples, d.s.c. run in a scanning mode from 25 to 210°C at 2.5°C min^{-1} heating rate for the measurement of residual reaction exotherm was carried out. The overall conversion can then be calculated as follows:

$$\alpha_s = \frac{\Delta H_{s,0} - \Delta H_{s,t}}{\Delta H_{s,0}} \qquad (1)$$

where α_s is the overall conversion for the partially cured sample at 110°C for reaction time t, $\Delta H_{s,0}$ is the total heat release from d.s.c. scanning run for the unreacted sample solution, and $\Delta H_{s,t}$ is the residual heat release from d.s.c. scanning run for the partially cured sample at 110°C for reaction time t.

The sample from each disc mould cured to various degrees of conversion was also pasted between two KBr plates and *FT*i.r. was employed to measure the conversions of styrene, polyester C=C bonds and overall C=C bonds. In addition, fractured surfaces of all the partially cured samples were characterized by SEM for their microstructures. Detailed conversion calculations of *FT*i.r. as well as SEM sample preparation procedures were given in the previous paper[13].

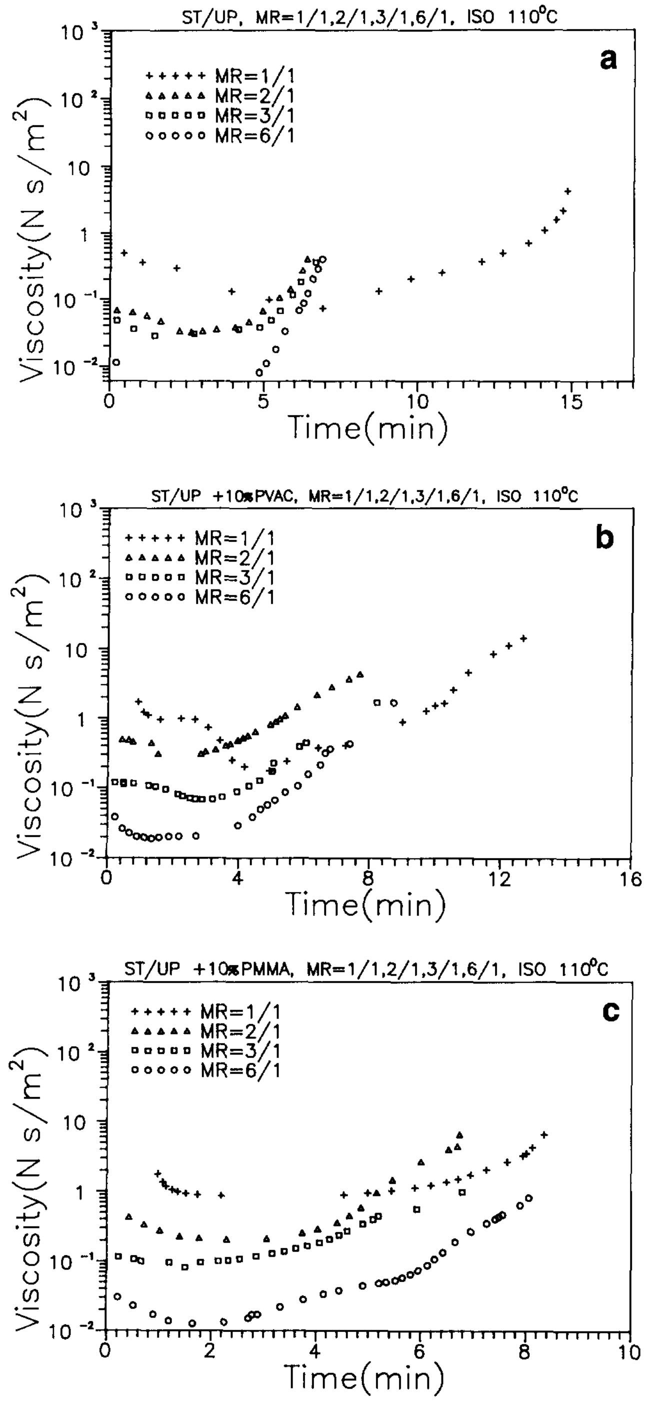

Figure 1 Viscosity variation vs. time profiles for UP resins with no LPA (a), with 10% PVAc (b), and with 10% PMMA (c), at various molar ratios of styrene to polyester C=C bonds cured at 110°C before gelation

RESULTS AND DISCUSSION

Rheokinetics

Figure 1 shows the viscosity variation vs. time profiles for UP resins containing no LPA, 10% PVAc and 10% PMMA, respectively, with $MR = 1/1$, 2/1, 3/1 and 6/1 during the cure at 110°C. It is seen that, for all three samples, the initial viscosity decreased with increasing molar ratio of styrene to polyester C=C bonds because of the styrene dilution effect. Also, at all molar ratios, the viscosity decreased with time up to a certain time, since the sample in the measuring unit was heated up from room temperature to 110°C, remaining unreacted, and the viscosity decreased as a result of increasing temperature. Once the sample started to cure, the viscosity increased with cure time and eventually exhibited a sharp increase near gelation. Since the time to reach infinite viscosity in *Figure 1* cannot be obtained accurately owing to the limitations of the instrument, to facilitate the determination of gelation time, the ratio of the initial viscosity to the viscosity during the cure was plotted against the cure time, as shown in *Figure 2* for all three samples. By extrapolating the viscosity ratio to zero, the gelation times can then be determined and are presented in *Table 1*. For all three samples, the gel time

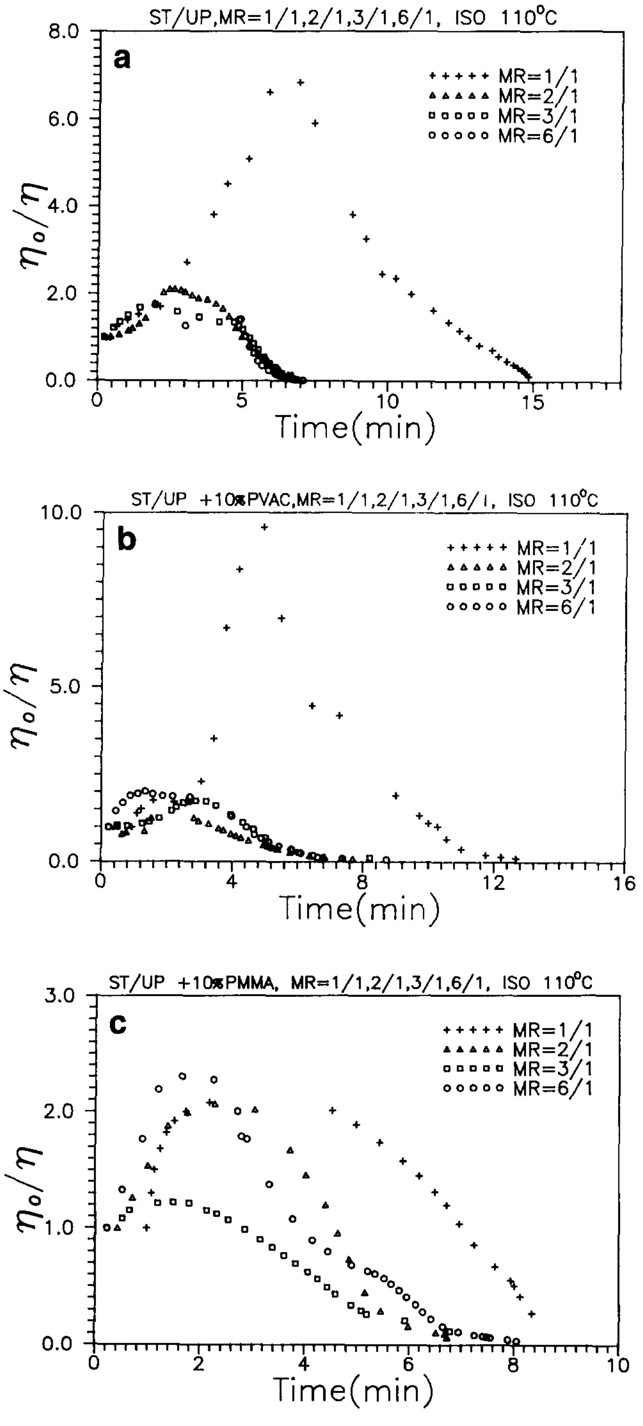

Figure 2 Ratio of the initial viscosity to the viscosity during the cure vs. time profiles for UP resins with no LPA (a), with 10% PVAc (b), and with 10% PMMA (c), at various molar ratios of styrene to polyester C=C bonds cured at 110°C before gelation

Table 1 Gel times and gel conversions for UP resins with no LPA, 10% PVAc and 10% PMMA at various molar ratios of styrene to polyester C=C bonds cured at 110°C

(a) Neat UP resin system

MR	1/1	2/1	3/1	6/1
t^*_{gel}[a] (min)	15.2±0.5	6.8±0.3	7.0±0.4	7.3±0.5
t^{H}_z (min)	6.9	2.6	1.5	2.5
t^{D}_z (min)	4.1	4.1	1.7	1.3
$t^*_{\mathrm{gel}}-t^{\mathrm{H}}_z+t^{\mathrm{D}}_z$	12.4	8.3	7.2	6.1
$\alpha^*_{\mathrm{gel,dsc}}$	0.32	0.03	0.04	0.11
$t^*_{\mathrm{gel}}-t^{\mathrm{H}}_z+t^{\mathrm{F}}_z$[b]	9.0	5.1	6.2	5.7
$\alpha^*_{\mathrm{gel,ftir}}$				
$\alpha^*_{\mathrm{gel,st}}$	0.71	0.22	0.17	0.05
$\alpha^*_{\mathrm{gel,pes}}$	0.53	0.32	0.18	0.05
$\alpha^*_{\mathrm{gel,tot}}$	0.62	0.25	0.17	0.05

(b) ST/UP/PVAc system

MR	1/1	2/1	3/1	6/1
t^*_{gel}[a] (min)	13.6±0.5	8.0±0.4	8.9±0.5	9.2±0.8
t^{H}_z (min)	5.0	2.8	3.0	1.4
t^{D}_z (min)	2.3	5.1	1.2	1.6
$t^*_{\mathrm{gel}}-t^{\mathrm{H}}_z+t^{\mathrm{D}}_z$	10.9	10.3	7.1	9.4
$\alpha^*_{\mathrm{gel,dsc}}$	0.04	0.11	0.12	0.13
$t^*_{\mathrm{gel}}-t^{\mathrm{H}}_z+t^{\mathrm{F}}_z$[b]	9.5	6.1	6.5	9.7
$\alpha^*_{\mathrm{gel,ftir}}$				
$\alpha^*_{\mathrm{gel,st}}$	0.58	0.34	0.43	0.30
$\alpha^*_{\mathrm{gel,pes}}$	0.57	0.41	0.49	0.68
$\alpha^*_{\mathrm{gel,tot}}$	0.58	0.36	0.45	0.35

(c) ST/UP/PMMA system

MR	1/1	2/1	3/1	6/1
t^*_{gel}[a] (min)	10.1±0.2	7.4±0.1	8.4±0.1	8.6±0.2
t^{H}_z (min)	3.3	2.7	1.5	1.6
t^{D}_z (min)	3.9	6.0	1.6	1.4
$t^*_{\mathrm{gel}}-t^{\mathrm{H}}_z+t^{\mathrm{D}}_z$	10.7	10.7	8.5	8.4
$\alpha^*_{\mathrm{gel,dsc}}$	0.03	0.02	0.10	0.22
$t^*_{\mathrm{gel}}-t^{\mathrm{H}}_z+t^{\mathrm{F}}_z$[b]	7.4	5.6	7.8	7.9
$\alpha^*_{\mathrm{gel,ftir}}$				
$\alpha^*_{\mathrm{gel,st}}$	0.37	0.095	0.22	0.10
$\alpha^*_{\mathrm{gel,pes}}$	0.35	0.15	0.28	0.17
$\alpha^*_{\mathrm{gel,tot}}$	0.36	0.11	0.24	0.12

[a] t^*_{gel} is the gel time measured by the Haake viscometer, t^{H}_z is the induction time revealed by the onset of viscosity rise in the measurement by the Haake viscometer, t^{D}_z is the induction time revealed by the d.s.c. reaction rate profile, and $\alpha^*_{\mathrm{gel,dsc}}$ is the corresponding gel conversion by comparison of rheological measurements and reaction conversion measurements by d.s.c. after correction for the induction time experienced by the sample in different instruments

[b] t^{F}_z is the induction time revealed by the *FT*i.r. conversion profile, and $\alpha^*_{\mathrm{gel,st}}$, $\alpha^*_{\mathrm{gel,pes}}$ and $\alpha^*_{\mathrm{gel,tot}}$ are the corresponding gel conversions for styrene, polyester C=C bonds and total C=C bonds, respectively, by comparison of rheological measurements and reaction conversion measurements by *FT*i.r. after correction for the induction time experienced by the sample in different instruments

was the longest at $MR=1/1$, followed by $MR=6/1$, 3/1 and 2/1. Among all the molar ratios, the gel time reached a minimum at $MR=2/1$, and either decreasing or increasing the molar ratio could raise the gel time. This phenomenon was also reported[1] for neat UP resins cured at 30°C.

The gel conversions can be obtained indirectly by comparison of the rheological measurement data here and the reaction conversion data measured by d.s.c., as shown in *Figure 3*, or by *FT*i.r. in the previous paper[13] on the same cure time basis. Since the amount of sample used was different in the measurements by d.s.c., *FT*i.r. and the Haake viscometer, being 6–10 mg, 0.8 mg and 2–3 g respectively, the induction times of the reaction carried out in the three instruments during the measurements were corrected for use in the gel conversion calculations. For the corresponding gel conversion based on the Haake viscometer and d.s.c., $\alpha^*_{\mathrm{gel,dsc}}$, the gel time employed was corrected as $t^*_{\mathrm{gel}}-t^{\mathrm{H}}_z+t^{\mathrm{D}}_z$, where t^*_{gel} is the gel time measured by the Haake viscometer, t^{H}_z is the induction time revealed by the onset of viscosity rise in the measurement by the Haake viscometer, and t^{D}_z is the induction time revealed by the d.s.c. reaction rate profile. Similarly, for the corresponding gel conversion based on the Haake viscometer and *FT*i.r., $\alpha^*_{\mathrm{gel,tot}}$ measured by *FT*i.r., the gel time employed was corrected as $t^*_{\mathrm{gel}}-t^{\mathrm{H}}_z+t^{\mathrm{F}}_z$, where t^{F}_z is the induction time revealed by the *FT*i.r. conversion profile. The estimated gel conversions for all three samples are listed in *Table 1*, where $\alpha^*_{\mathrm{gel,tot}}$ measured by *FT*i.r. was generally larger than $\alpha^*_{\mathrm{gel,dsc}}$ at all molar ratios. For example, for UP resins at $MR=2/1$ with no LPA, 10% PVAc and 10% PMMA, the gel conversions estimated by d.s.c. were 3%, 11% and 2%, respectively, whereas those estimated by *FT*i.r. were 25%, 36% and 11%, respectively. For UP resins with no LPA and 10% PMMA, among all the molar ratios, $\alpha^*_{\mathrm{gel,dsc}}$ reached a minimum at $MR=2/1$. Either decreasing or increasing the molar ratio could raise the estimated gel conversion, $\alpha^*_{\mathrm{gel,dsc}}$. The same trend of variation in $\alpha^*_{\mathrm{gel,tot}}$ measured by *FT*i.r. with the molar ratio of styrene to polyester C=C bonds was also found[1] for neat UP resins cured at 30°C. For other comments on conversion vs. styrene-to-fumarate ratio, the reader is referred to the work of Boenig[14]. However, for the UP resins with 10% PVAc, $\alpha^*_{\mathrm{gel,dsc}}$ increased with increasing molar ratio.

In order to know the accuracy of the estimated gel conversions, partially cured samples up to gelation for UP resins at $MR=2/1$ with no LPA, 10% PVAc and 10% PMMA cured at 110°C were quenched in liquid nitrogen to stop any further reaction. The viscosity, reaction conversions and microstructure for the fractured sample surface were measured or observed at room temperature. *Figure 4* shows the viscosity variations with time, where the viscosity of the partially cured sample near gelation was 164, 42 and 26 times as high as the initial viscosity for the UP resins with no LPA, 10% PVAc and 10% PMMA respectively (also see *Table 2*). The viscosity and reaction conversions measured by d.s.c. and *FT*i.r. corresponding to each sampling point in *Figure 4* for the three samples are also displayed in *Table 2*, where the last column lists the true gel gime, gel conversion of total C=C bonds measured by d.s.c., and gel conversions of styrene, polyester C=C bonds and total C=C bonds measured by *FT*i.r.. These were obtained by plotting the viscosity ratio, η_0/η, vs. time, d.s.c. conversion and *FT*i.r. conversion, respectively, followed by extrapolating the corresponding curve to zero viscosity ratio. The data in *Table 2* reveal that, for all three samples, the conversions of total C=C bonds measured by both d.s.c. and *FT*i.r. (i.e. α_{s} and α_{tot}) generally showed good agreement. The conversion of polyester C=C bonds, α_{pes}, always exceeded that of styrene, α_{st}, before or right after gelation, and the gel conversion was about 8.9–9.3%, 11–13% and 15.5–20% for the UP resins with no LPA, 10% PVAc and 10% PMMA, respectively. When compared with the gel conversion data at $MR=2/1$ shown in *Tables 1* and *2*, it is seen that, except for the PVAc-containing sample, the gel conversion obtained indirectly by d.s.c.

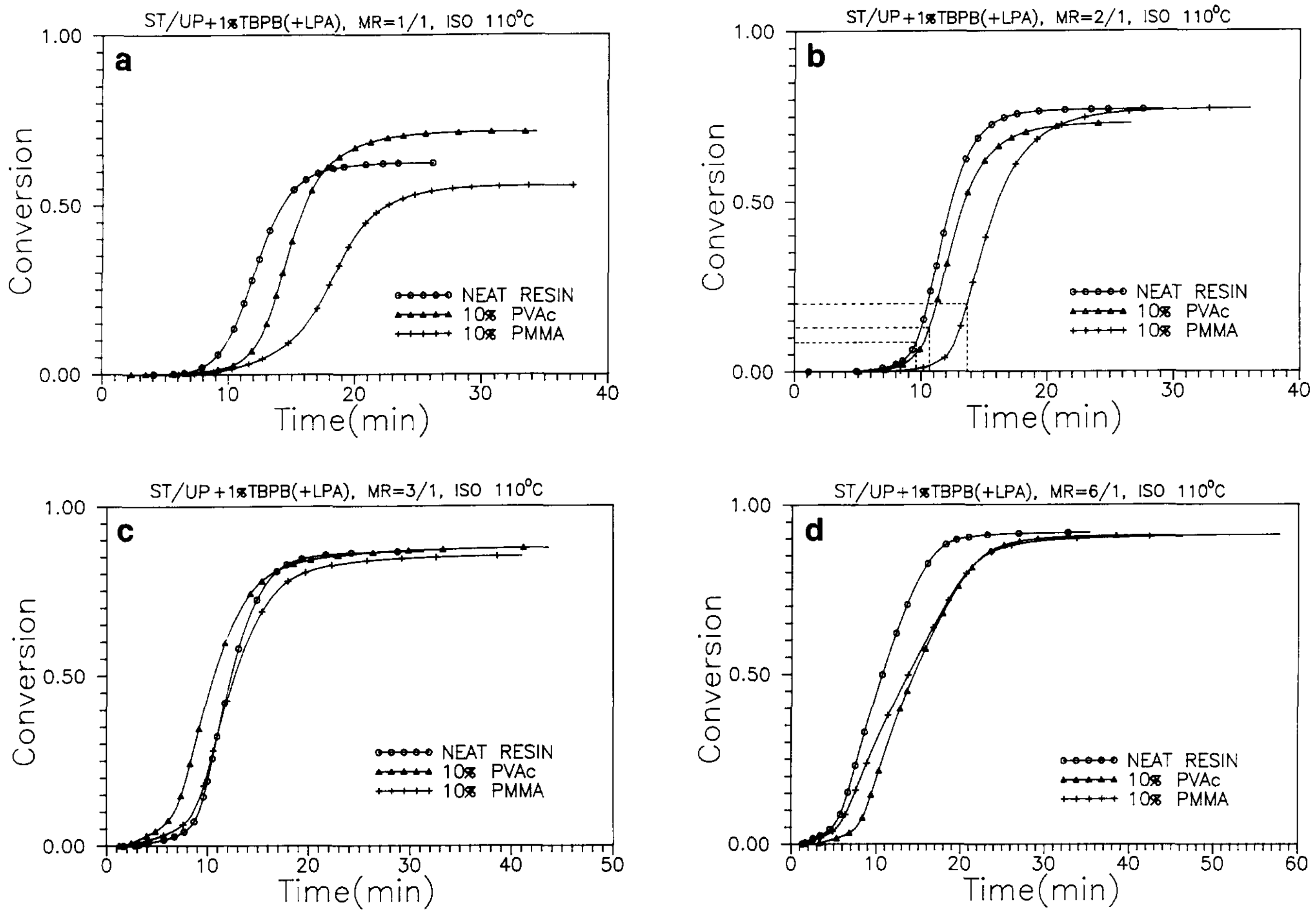

Figure 3 D.s.c. overall conversion profiles for UP resins containing no LPA, 10% PVAc and 10% PMMA with various molar ratios of styrene to polyester C=C bonds cured isothermally at 110°C: (a) $MR=1/1$, b) $MR=2/1$, (c) $MR=3/1$ and (d) $MR=6/1$. The gel times corresponding to the true gel conversions at $MR=2/1$ shown in *Table 2* are designated, which are 9.7 min, 10.8 min and 13.8 min for the UP resins with no LPA, 10% PVAc and 10% PMMA respectively

underestimated the true value (3% vs. 8.9–9.3%, 11% vs. 11–13% and 2% vs. 15.5–20% for the UP resins with no LPA, 10% PVAc and 10% PMMA, respectively), while, except for the PMMA-containing sample, the gel conversion obtained indirectly by *FT*i.r. overestimated it (25% vs. 8.9–9.3%, 36% vs. 11–13% and 11% vs. 15.5–20% for UP resins with no LPA, 10% PVAc and 10% PMMA, respectively). In other words, the gel conversion data by indirect comparison of rheological changes and overall conversion variations by either d.s.c. or *FT*i.r. on the same cure time basis could deviate greatly from the true ones by direct measurements for partially cured samples near gelation. Nevertheless, the gel time measured directly during the cure at 110°C showed very good agreement with that obtained from the viscosity rise curve for partially cured samples measured at room temperature (6.8 vs. 6.4 min, 8.0 vs. 7.16 min and 7.4 vs. 7.45 min for the UP resins with no LPA, 10% PVAc and 10% PMMA, respectively).

The true gel times and gel conversion data for the UP resins at $MR=2/1$ with no LPA, 10% PVAc and 10% PMMA cured at 110°C, as listed in the last column of *Table 2*, reveal that adding LPA to neat UP resin could increase both the gel time and the gel conversion. Also, UP resin with PMMA exhibited longer gel time and higher gel conversion than that with PVAc. When the gel conversion, α_s, measured directly by d.s.c. was designated on the d.s.c. overall conversion profile at $MR=2/1$ shown in *Figure 3b*, the corresponding gel times on the basis of d.s.c. cure were found to be 9.7 min, 10.8 min and 13.8 min for the UP resins with no LPA, with 10% PVAc and with 10% PMMA, respectively. The trend of order of gel times for the three samples remains the same as that in *Table 2* (i.e. PMMA > PVAc > neat UP resin). The corresponding location on the d.s.c. reaction rate profile at gelation, as shown in *Figure 5*, was generally around midway of the sharp rise portion of the rate profile prior to the maximum peak.

Morphology

Neat UP resin system. The microstructures of fractured surfaces for the partially cured neat UP samples corresponding to *Figure 4a* (or points in *Table 2a*) are shown in *Figure 6*. *Figure 6a*, point 1 of *Figure 4a*, was at a conversion of $\alpha_s=1.9\%$. At a magnification of 1000 ×, it can be seen that microgel particles are scattered around at the bottom part of the picture. At the upper right and lower right corners of the picture, many microgel particles are seen to be somewhat closely overlapped, while around the central part of the picture, many microgel particles are seen to be fused together. At a magnification of 5000 ×, the size of the microgel particles appears slightly non-uniform, and ranges from 0.5 μm to 2.3 μm. *Figure 6b*, point 2 of *Figure 4a*, was at a conversion of $\alpha_s=8.0\%$. At a magnification of 1000 ×, it shows a

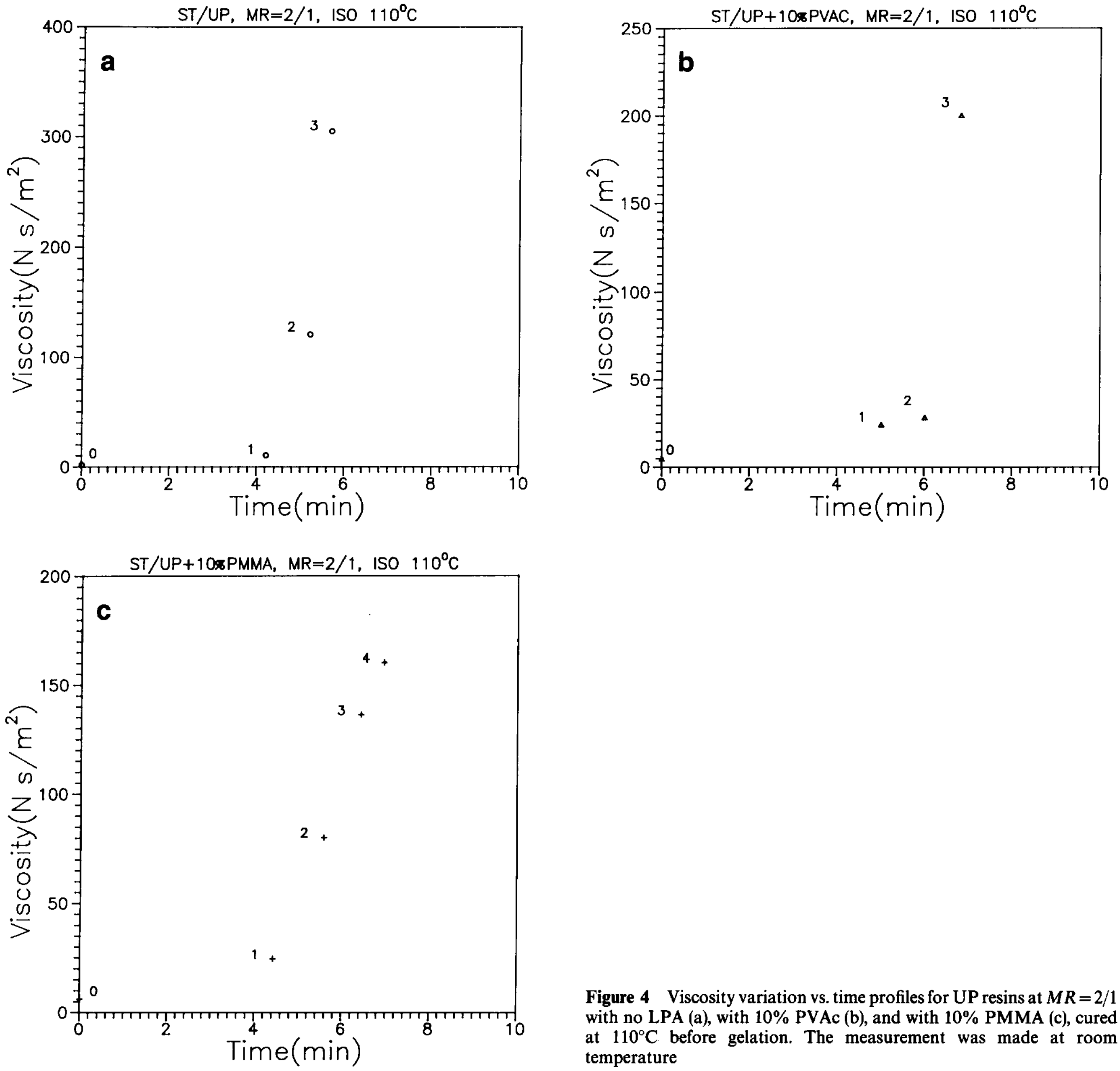

Figure 4 Viscosity variation vs. time profiles for UP resins at $MR=2/1$ with no LPA (a), with 10% PVAc (b), and with 10% PMMA (c), cured at 110°C before gelation. The measurement was made at room temperature

fluid-like, loose microstructure. At a magnification of 5000 ×, vague microgel particles seem to be fused together locally and form the microstructure seen at 1000×. *Figure 6c*, point 3 of *Figure 4a*, was at a conversion of $\alpha_s=8.3\%$. It reveals a similar microstructure to that in *Figure 6b*, but vague microgel particles that are locally fused together tend to percolate through the system. As a matter of fact, the sample at this point pretty much approaches the gelation state. *Figure 6d*, point 4 in *Table 2a*, was at a conversion of $\alpha_s=11.4\%$ and right after the gel point ($\alpha_s=8.9\%$). The microstructure at a magnification of 1000× turns out to be slightly more compact than that in *Figure 6c'*.

ST/UP/PVAc system. The microstructures of fractured surfaces for the partially cured UP samples with 10% PVAc corresponding to *Figure 4b* (or points in *Table 2b*) are shown in *Figure 7*. *Figure 7a*, point 1 of *Figure 4b*, was at a conversion of $\alpha_s=1.38\%$. At a magnification of 1000×, microgel particles generated in local spots are seen to be distributed in most of the sample surface. At a magnification of 5000 ×, a number of microgel particles, with an average diameter of 0.9 μm, are seen to be fused together locally and form a loose, global network structure. *Figure 7b*, point 2 in *Figure 4b*, was at a conversion of $\alpha_s=1.66\%$. The microstructure appears slightly more compact than that in *Figure 7a* at a magnification of 1000×. At a magnification of 5000×, the microgel particles generated are greater in number and less fused with each other. *Figure 7c*, point 3 in *Figure 4b*, was at a conversion of $\alpha_s=9.64\%$ and quite close to the gelation point ($\alpha_s=13\%$). At a magnification of 1000×, the microgel particles generated turn out to be clearly identified, and tend to percolate through the whole system. At a magnification of 5000 ×, the microgel particles, about 1.2 μm in diameter, are seen to be even greater in number, slightly fused with each other and connected into a somewhat dense network. *Figure 7d*, point 4 in *Table 2b*, was at a conversion of $\alpha_s=21.03\%$ and well over the gelation point. The microgel particles

Table 2 The viscosity and reaction conversions for the partially cured samples up to gelation for UP resins at $MR=2/1$ with no LPA, 10% PVAc and 10% PMMA cured at 110°C. The measurements were carried out at room temperature for the sampling points as designated in *Figure 4*

(a) Neat UP resin system

Point	0	1	2	3	4	Gel point[a]
t (min)	0	4.22	5.32	6.17	7.00	6.40
Viscosity, η (N s m^{-2})	1.85	10.42	120.51	304.46	solid	∞
η_0/η	1	0.178	0.0154	0.0061	–	0
D.s.c. conv.[b]						
α_s	0	0.019	0.080	0.083	0.114	0.089
*FT*i.r. conv.						
α_{st}	0	0.043	0.076	0.086	0.101	0.090
α_{pes}	0	0.052	0.094	0.093	0.112	0.098
α_{tot}	0	0.046	0.082	0.089	0.105	0.093

(b) ST/UP/PVAc system

Point	0	1	2	3	4	Gel point
t (min)	0	5.01	6.14	6.92	7.21	7.16
Viscosity, η (N s m^{-2})	4.81	24.04	28.04	200.03	solid	∞
η_0/η	1	0.200	0.172	0.0240	–	0
D.s.c. conv.						
α_s	0	0.014	0.017	0.096	0.210	0.130
*FT*i.r. conv.						
α_{st}	0	0.020	0.039	0.086	0.183	0.10
α_{pes}	0	0.030	0.044	0.098	0.186	0.13
α_{tot}	0	0.023	0.041	0.090	0.184	0.11

(c) ST/UP/PMMA system

Point	0	1	2	3	4	5	Gel point
t (min)	0	4.22	5.69	6.51	7.22	7.7	7.45
Viscosity, η (N s m^{-2})	5.7	24.46	80.10	136.21	160.24	solid	∞
η_0/η	1	0.250	0.076	0.045	0.038	–	0
D.s.c. conv.							
α_s	0	0.036	0.043	0.114	0.150	0.29	0.20
*FT*i.r. conv.							
α_{st}	0	0.032	0.049	0.099	0.124	0.184	0.150
α_{pes}	0	0.052	0.064	0.110	0.139	0.190	0.164
α_{tot}	0	0.039	0.054	0.102	0.136	0.186	0.155

[a] The last column lists the true gel time, gel conversion of total C=C bonds measured by d.s.c., and gel conversions of styrene, polyester C=C bonds and total C=C bonds measured by *FT*i.r., which were obtained by plotting the viscosity ratio, η_0/η, vs. time, d.s.c. conversion and *FT*i.r. conversion, respectively, followed by extrapolating the corresponding curve to zero viscosity ratio

[b] α_s is the conversion of total C=C bonds measured directly by d.s.c. for the partially cured sample; α_{st}, α_{pes} and α_{tot} are the conversions of styrene, polyester C=C bonds and total C=C bonds, respectively, measured directly by *FT*i.r. for the partially cured sample

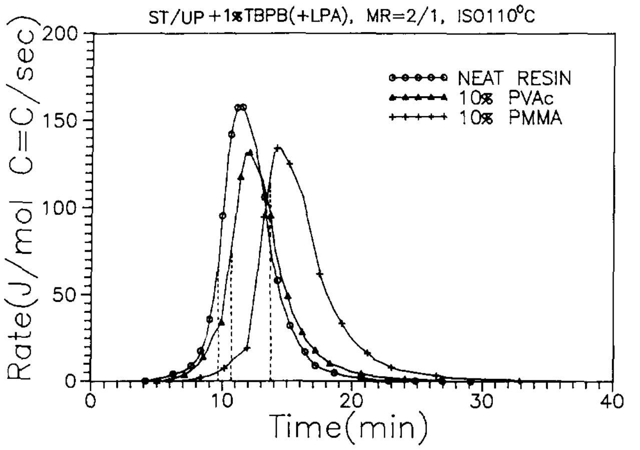

Figure 5 D.s.c. reaction rate profiles for UP resins at $MR=2/1$ containing no LPA, 10% PVAc and 10% PMMA cured isothermally at 110°C. The true gelation points are designated (see text)

generated are greater in number, closely overlapped with other, more compact and more conspicuous in their spherical outlines.

ST/UP/PMMA system. The microstructures of fractured surfaces for the partially cured UP samples with 10% PMMA corresponding to *Figure 4c* (or points in *Table 2c*) are shown in *Figure 8*. *Figure 8a*, point 1 of *Figure 4c*, was at a conversion of $\alpha_s=3.6\%$. At a magnification of 2000×, it shows a loose, fluid-like microstructure. At a magnification of 5000×, many holes that are scattered around can be clearly identified, which are presumably due to materials in the PMMA dispersed phase being washed off. In contrast, the continuous phase reveals a swollen microstructure, which is composed of many vague and soft microgel particles somewhat overlapped with each other. *Figure 8b*, point 2 in *Figure 4c*, was at a conversion of $\alpha_s=4.29\%$. The overall

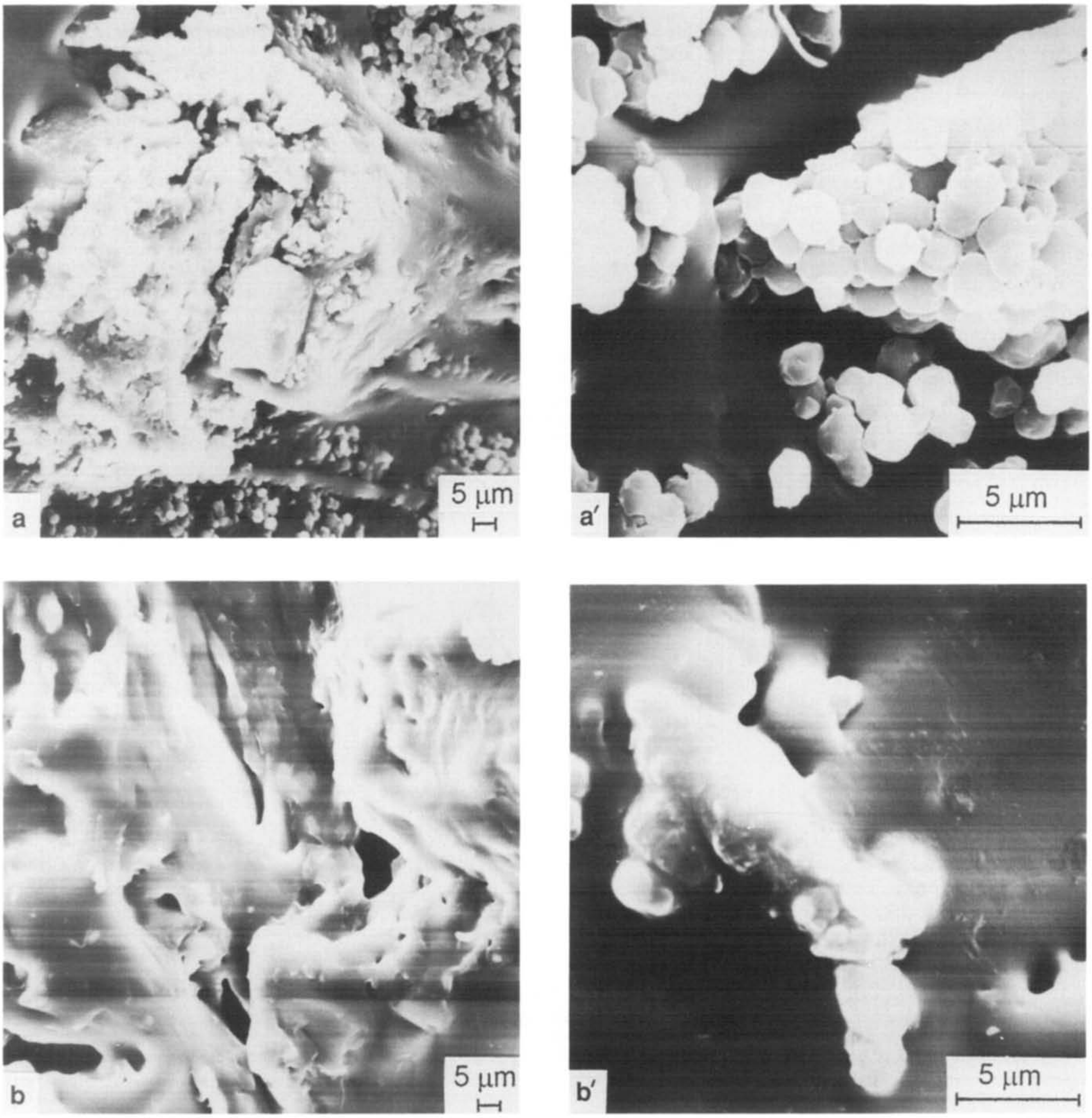

Figure 6 SEM micrographs of fractured surfaces for neat UP resins with $MR=2/1$ cured at 110°C for the points shown in *Figure 4a* or *Table 2a* with various conversion levels measured by d.s.c.: (a) $\alpha_s=1.88\%$, (b) $\alpha_s=8.0\%$, (c) $\alpha_s=8.34\%$ and (d) $\alpha_s=11.4\%$; (a), (b) and (d) obtained at 1000 × and 5000 ×, (c) at 500 × and 1000 ×

microstructure appears more viscous fluid-like at a magnification of 1000 ×. At a magnification of 5000 ×, the continuous phase is characterized by many slightly compact blocks, which result from the close overlapping of a great number of vague and soft microgel particles in local spots. A few holes still exist in between the blocks. *Figure 8c*, point 3 in *Figure 4c*, was at a conversion of $\alpha_s=11.36\%$. A loose, flake-like microstructure is formed in the crosslinked UP continuous phase by connecting the local blocks, shown in the previous picture, together as the crosslinking reaction progresses, while the PMMA dispersed phase is characterized by a few holes with non-uniform size distribution. At a magnification of 600 ×, there seem to be some microgel particles appearing on the wall of the hole for the PMMA dispersed phase. *Figure 8d*, point 4 in *Figure 4c*, was at a conversion of $\alpha_s=15.0\%$ and quite close to the gel point ($\alpha_s=20.0\%$). At a magnification of 300 ×, the global phase separation phenomenon is pronounced since many holes pertaining to the PMMA dispersed phase are distributed quite uniformly in the system. At a magnification of 2000 ×, the microgel particles emerging from the wall of holes in the PMMA dispersed phase are evident, while the crosslinked UP continuous phase exhibits a flake-like microstructure. *Figure 8e*, point 5 in *Table 2c*, was at a conversion of $\alpha_s=29.0\%$ and well over the gelation point. The PMMA dispersed phase is full of many clearly identified microgel particles that are intimately

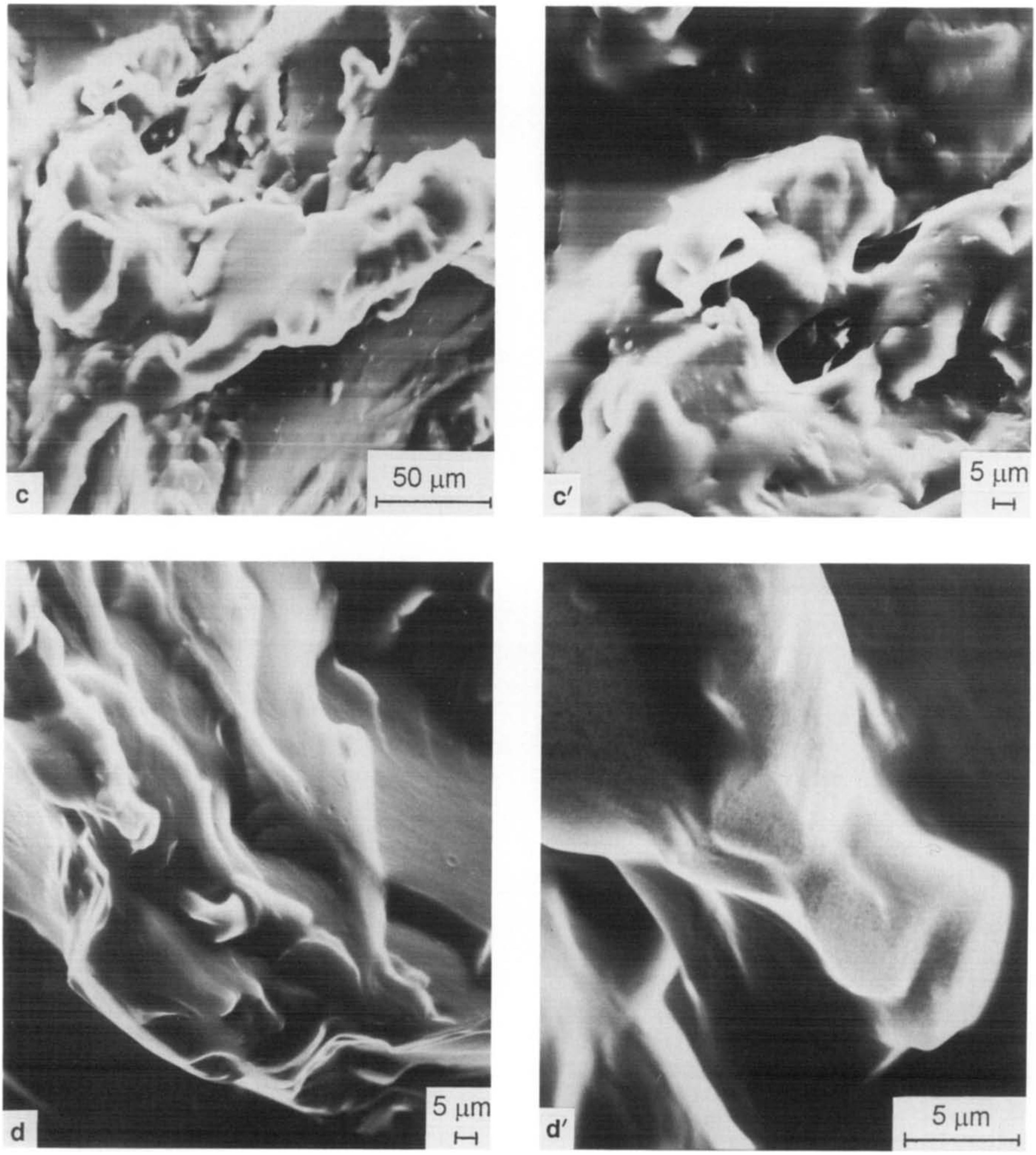

Figure 6 *continued*

overlapped with each other, and the crosslinked UP continuous phase forms a compact, slightly oriented flake-like microstructure. By referring to *Figures 3b* and *5*, such a reaction conversion level corresponds to around the maximum point in the d.s.c. reaction rate profile shown in *Figure 5*. Many microvoids and microcracks responsible for the volume shrinkage control can also be observed in the PMMA dispersed phase as shown in *Figure 8e*.

For the action of LPA in the cure of UP resins the reader could also be referred to the pioneer work of Pattison *et al.*[15,16], in which a morphology of crosslinked beads (microgels) and fissures/cracks in the thermoplastic-rich phase is described.

Microgel-based gelation mechanism

Based on the observation of morphological changes up to gelation for UP resins with and without LPA shown in *Figures 6–8*, a microgel-based gelation mechanism in the isothermal cure of UP resins at 110°C can be elucidated as follows. The microgel particles would be

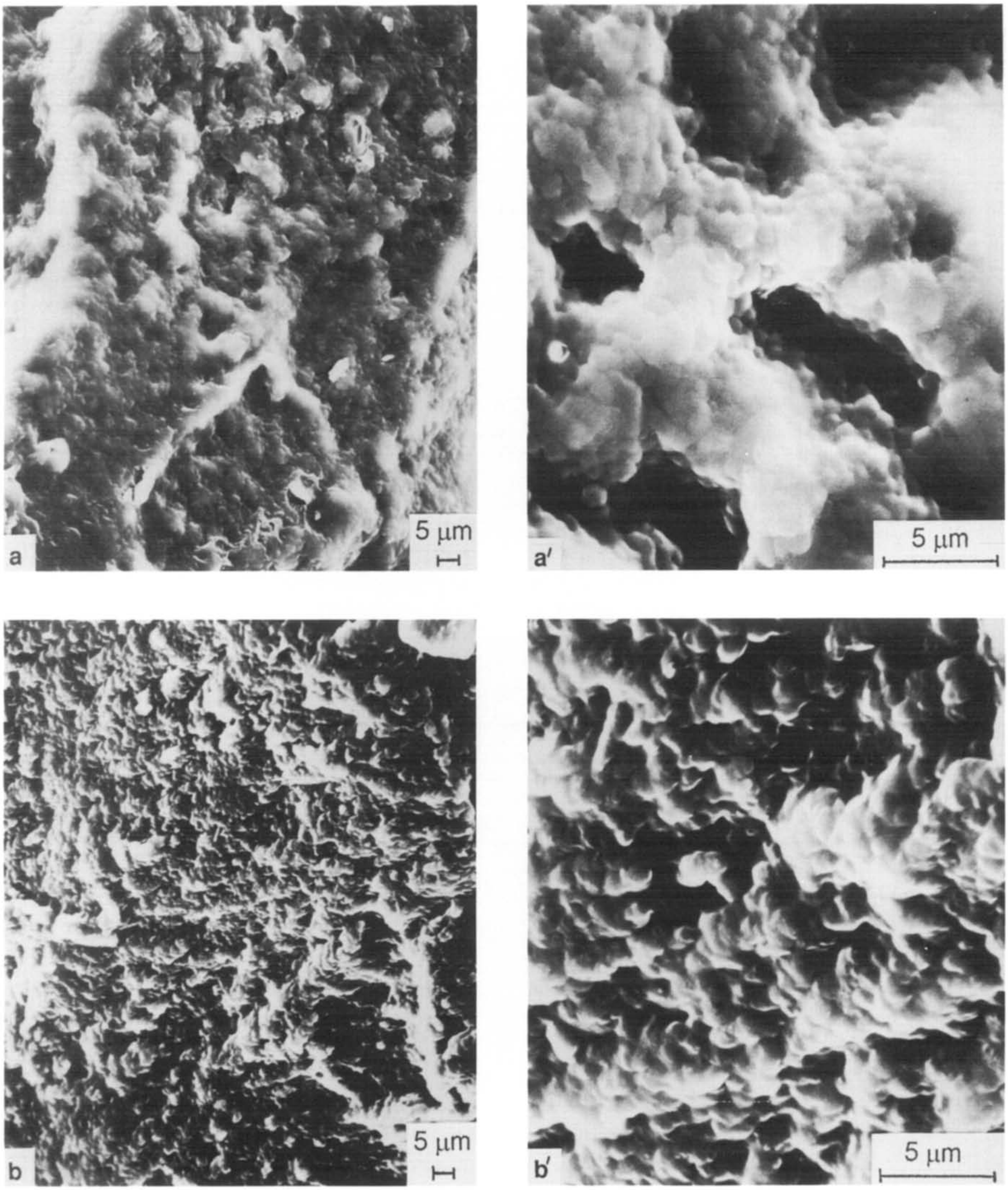

Figure 7 SEM micrographs of fractured surfaces for UP resins with $MR = 2/1$ containing 10% PVAc cured at 110°C for the points shown in *Figure 4b* or *Table 2b* with various conversion levels measured by d.s.c.: (a) $\alpha_s = 1.38\%$, (b) $\alpha_s = 1.66\%$, (c) $\alpha_s = 9.64\%$ and (d) $\alpha_s = 21.03\%$; micrographs obtained at 1000 × and 5000 ×

generated continuously from the beginning of the reaction. Prior to 5% reaction conversion, where the concentration of microgel particles generated is not too high, the intramicrogel crosslinking reaction would predominate over the intermicrogel crosslinking one, and the system viscosity could go up to at most 4–6 times as high as the initial viscosity, as shown in point 1 of *Table 2*. This is because the build-up of network structure is limited to some local spots. As the reaction progresses to 5–10% conversion, more and more microgel particles would be generated, so that the intermicrogel crosslinking reaction could occur to an appreciable extent, leading to a gradual spanning of the network structure build-up through the system. A rapid increase of the system

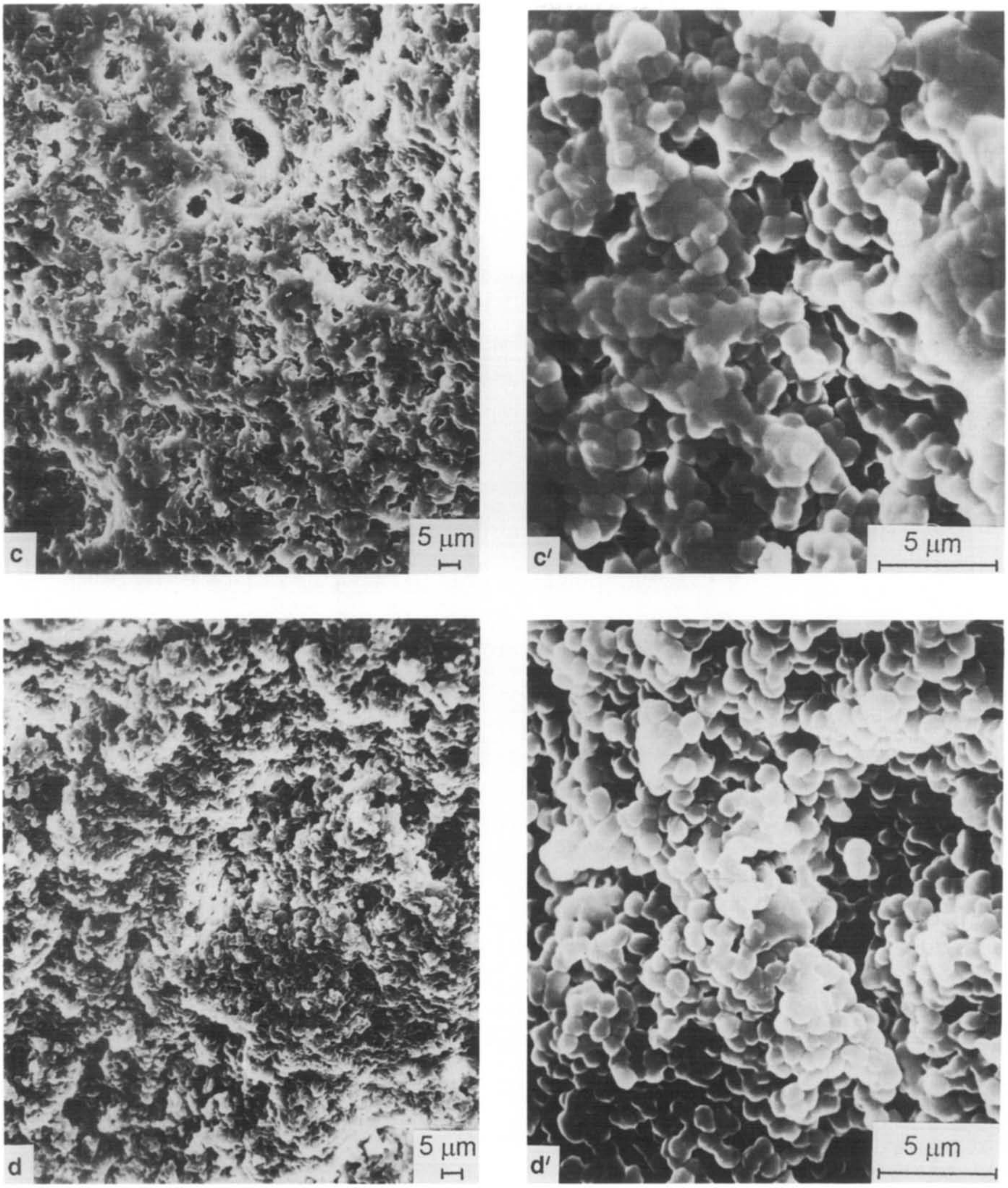

Figure 7 *continued*

viscosity to tens or a few hundreds of times as high as the initial viscosity could thus arise, as shown in points 2 and 3 of *Table 2*. At a reaction conversion of 9–20%, gelation is reached, where the microgel particles generated would percolate through the system via the intermicrogel crosslinking reactions for the first time and the system viscosity could then increase to infinity. Although the microgel particles may not be clearly identified at gelation, such as for the neat UP resin and the UP resin containing 10% PMMA systems as shown in *Figures 6c* and *8d*, the gelation mechanism would be essentially dominated by chemical crosslinking of microgel particles (i.e. intermicrogel crosslinking) for UP resins either with or without LPA.

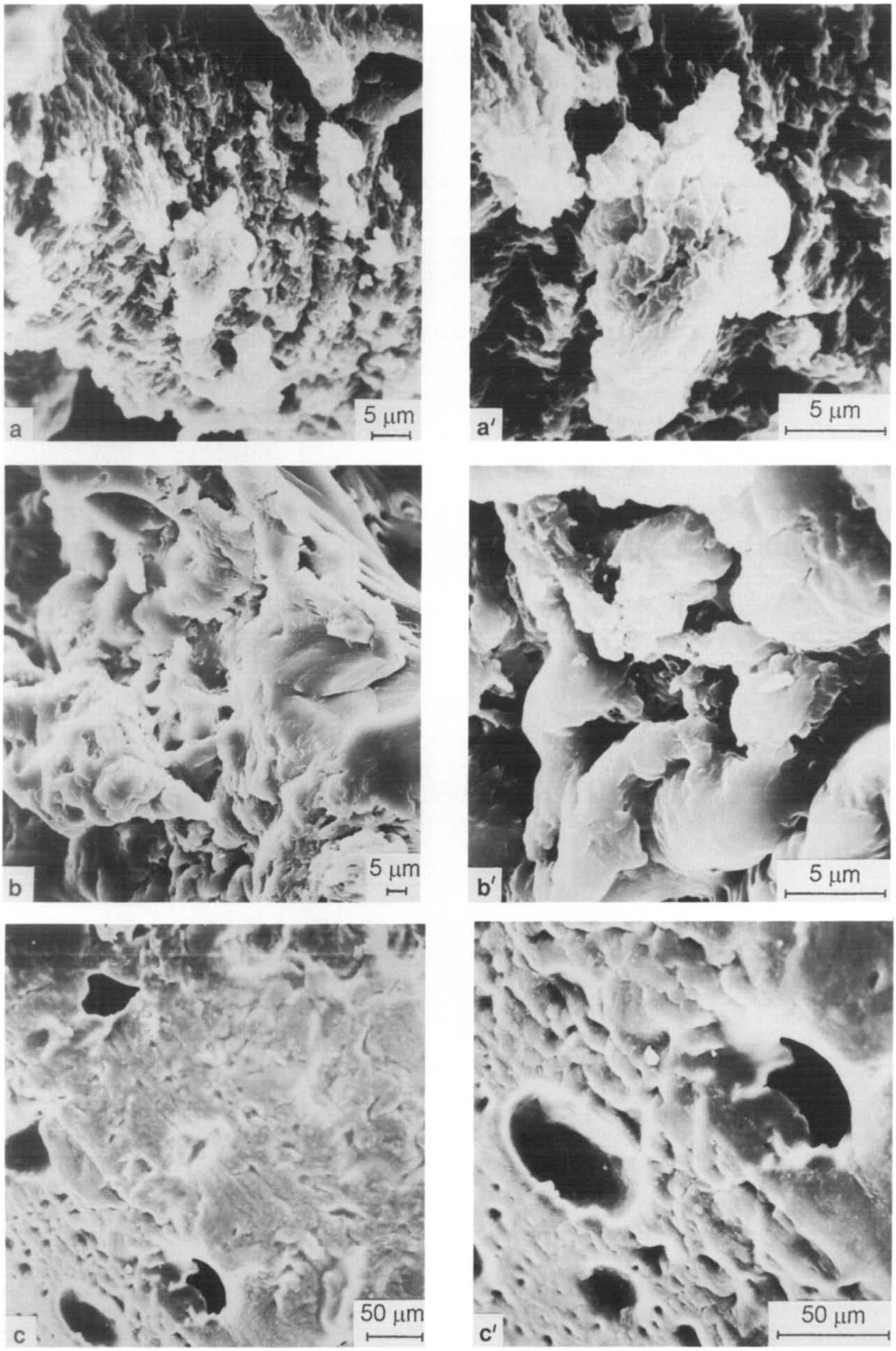

Figure 8 SEM micrographs of fractured surfaces for UP resins with $MR = 2/1$ containing 10% PMMA cured at 110°C for the points shown in *Figure 4c* or *Table 2c* with various conversion levels measured by d.s.c.: (a) $\alpha_s = 3.6\%$, (b) $\alpha_s = 4.29\%$, (c) $\alpha_s = 11.36\%$, (d) $\alpha_s = 15.0\%$ and (e) $\alpha_s = 29\%$; (a) obtained at 2000 × and 5000 ×, (b) at 1000 × and 5000 ×, (c) at 300 × and 600 ×, (d) at 300 × and 2000 ×, and (e) at 1000 × and 2500 ×

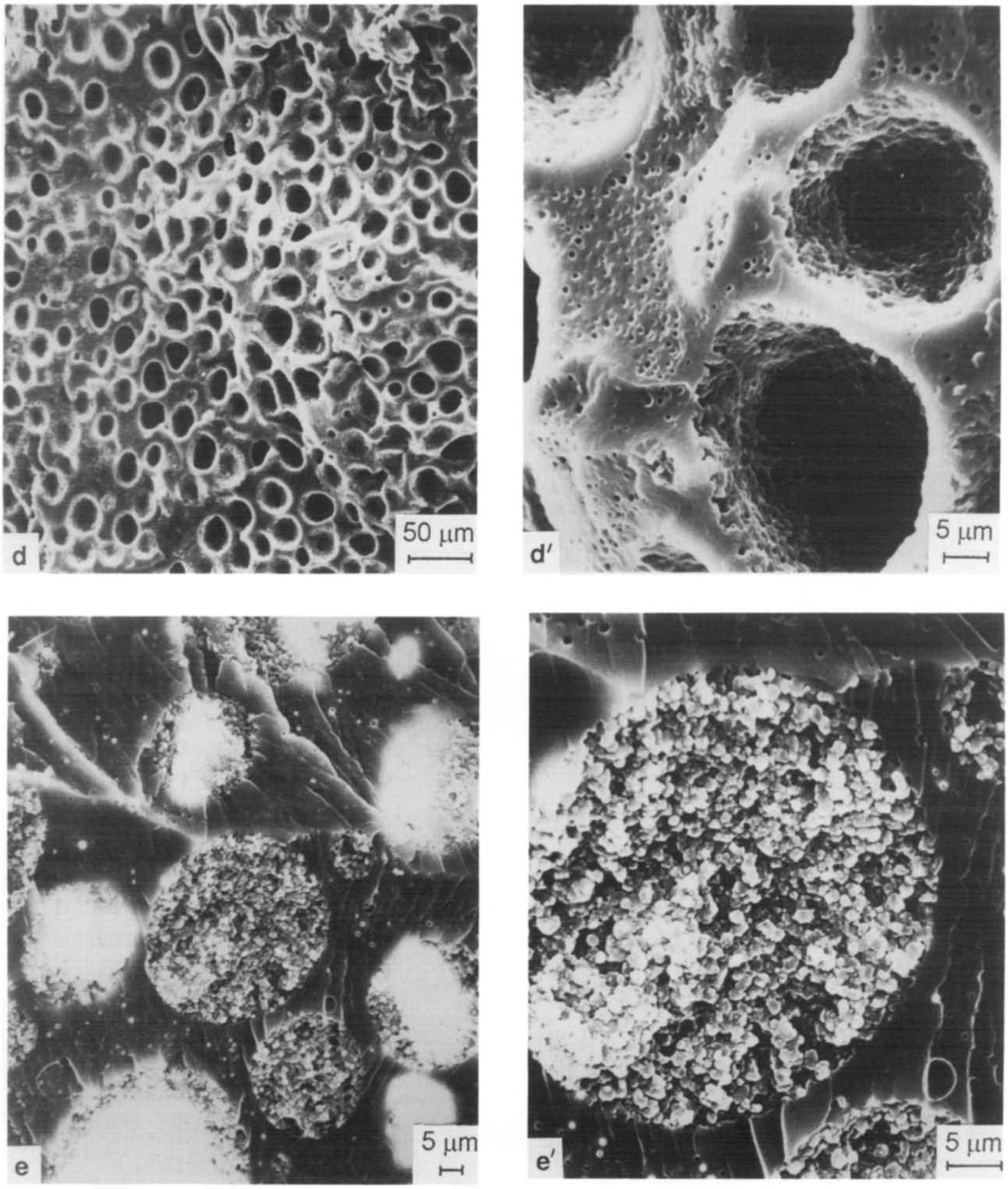

Figure 8 *continued*

Effects of LPA-enhanced phase separation on gelation

In the cure of UP resins with LPA, microgel particles generated are allowed to be clearly identified. This is because a layer of LPA could cover the surface of the microgel particle as a result of the phase separation of microgel particles from the unreacted resin matrix containing LPA. The segregating effect of LPA on microgel particles could enhance the subsequent intramicrogel crosslinking reactions[13]. Since the wasteful monomer conversion due to the LPA-enhanced intramicrogel crosslinking reactions would contribute little to the macrogelation, which would depend on the build-up of network structure mainly contributed by the intermicrogel crosslinking reactions, adding LPA to the neat UP resins could delay the gel time and increase the gel conversion as mentioned earlier. It should be noted that the delay of gel time could also be partly attributed to a decrease of the intermicrogel crosslinking reaction rate caused by LPA[13].

Our previous study of phase characteristics for styrene/UP/LPA systems showed that PVAc is a compatible LPA with the uncured UP resins at $MR = 2/1$, while PMMA is an incompatible one. For the PVAc-containing sample, the microgel particles are seen to be uniformly distributed throughout the system before the gelation point, as shown in *Figures 7a–c*. In contrast, for the PMMA-containing sample, the global phase separation results in a crosslinked UP continuous phase and a PMMA dispersed phase prior to the gelation point, as shown in *Figures 8a–d*. Based on the ternary static phase characteristics at 25°C[13], during the cure of UP resins at $MR=2/1$ with 10% PMMA, the dispersed phase would be PMMA-rich and the molar ratio of styrene to polyester C=C bonds would be $MR>2/1$ (i.e. styrene-rich), whereas the continuous phase would be PMMA-lean with $MR<2/1$ (i.e. styrene-lean). Therefore, microgel particles generated in the continuous phase tend to be merged together and lose the identity of microgel particles owing to the inadequate segregating effects of both PMMA and styrene on them at the early stage of the reaction, as shown in *Figures 8a* and *8b*. As the reaction goes on, the microstructure in the continuous phase appears flake-like near gelation owing to the close overlapping of microgel particles, as shown in *Figures 8c* and *8d*. In contrast, clearly identified microgel particles could be easily observed in the PMMA dispersed phase owing to the better segregating effects of both PMMA and styrene on microgel particles, as shown in *Figures 8c–e*. At gelation, as shown in *Figure 8d*, the continuous phase gels, while the dispersed phase lags behind, which may presumably be caused by too high a molar ratio of styrene to polyester C=C bonds (the rate of self-bonding of styrene being less than that of copolymerization between styrene and polyester C=C bonds[17]). Therefore, the intramicrogel crosslinking reactions in both the continuous and the dispersed phases would lead to an even higher wasteful monomer conversion, which could not contribute to macrogelation in the continuous phase, as compared with that of the PVAc-containing sample, which is characterized by a co-continuous phase consisting of a crosslinked UP phase (i.e. microgel particles) and a PVAc phase, with essentially no other phase-separated regions containing UP and styrene monomers. As a consequence, the gel conversion for the PMMA-containing sample is higher than that for the PVAc-containing sample.

Again, based on the ternary static phase characteristics at 25°C, the molar ratio of styrene to polyester C=C bonds in the continuous phase, which will gel first as mentioned earlier, is lower for the PMMA-containing sample than that for the PVAc-containing sample ($MR=1.27$ vs. $MR=1.79$)[13]. Hence, in the continuous phase to be gelled, the rate of intramicrogel crosslinking reactions, which include the formation of microgel particles and the subsequent crosslinking reactions inside the microgel particles, would be lower for the PMMA-containing sample during the cure at 110°C prior to gelation owing to an inadequate styrene swelling effect as compared with the PVAc-containing sample[18], provided that the initiator concentration would not be redistributed between the continuous phase and the dispersed phase as a result of phase separation. As mentioned earlier, gelation is where the microgel particles generated percolate through the reaction system for the first time. Thus, the lower the microgel formation rate, the longer the gel time. A longer gel time for the PMMA-containing sample results accordingly.

CONCLUSIONS

Care should be taken in obtaining true gel conversions since the gel conversion data by indirect comparison of rheological changes and overall conversion variations by either d.s.c. or *FT*i.r. on the same cure time basis could deviate greatly from the true ones by direct measurements for partially cured samples near gelation. For the UP resins with $MR=2/1$ cured isothermally at 110°C, the true gel conversions are at a level of 8.9–9.3%, 11–13% and 15.5–20% for UP resins with no LPA, with 10% PVAc and with 10% PMMA, respectively. The true gelation point would be generally located around midway of the sharp rise portion of the d.s.c. reaction rate profile prior to the maximum peak.

The gelation mechanism would be dominated by chemical crosslinking of microgel particles (i.e. intermicrogel crosslinking) in the cure of UP resins either with or without LPA. Adding LPA in the neat UP resins could delay the gel time and increase the gel conversion. This is mainly because the wasteful monomer conversion due to the LPA-enhanced intramicrogel crosslinking reactions would contribute little to the macrogelation, which would depend on the build-up of network structure mainly contributed by the intermicrogel crosslinking reactions. The UP resin with a compatible LPA, such as PVAc, shows a shorter gel time and a lower gel conversion than that with an incompatible LPA, such as PMMA, which can be elucidated by the ternary static phase characteristics of styrene/UP/LPA systems at 25°C.

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