Microstructure formation in the cure of unsaturated polyester resins

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The microstructures in cured styrene–unsaturated polyester resins were studied by using scanning electron microscopy. The size and structure of the microgels depend strongly on the concentration of styrene monomer and the chemical structure of the polyester resins. Using a Fourier-transform infra-red spectroscopic method, changes of styrene and polyester vinyl groups during reaction were measured. The results revealed that microgel formation has a great effect on the reaction kinetics of unsaturated polyester resins.

(Keywords: microgel particle; unsaturated polyester resin; morphology; scanning electron microscopy; Fourier-transform infra-red spectroscopy)

INTRODUCTION

The most widely used thermoset resins are polyesters[1]. Thermoset polyesters, while relatively inexpensive, offer advantages such as light weight, high strength and excellent mechanical properties. With the aid of fillers, reinforcements and additives, they are usually available in the form of compounds for compression moulding (e.g. sheet moulding compound, SMC), injection moulding (e.g. bulk moulding compound, BMC), resin transfer moulding and pultrusion.

The reaction of unsaturated polyester resin is a free-radical chain-growth copolymerization between the styrene monomer and the unsaturated polyester molecule. Polyester molecules are the crosslinkers while styrene serves as an agent to link the adjacent polyester molecules.

Several researchers have studied the reaction mechanism of unsaturated polyester resins. Horie and coworkers[2,3] carried out a detailed experimental study using differential scanning calorimetry (d.s.c.). They found that network formation due to the presence of highly unsaturated resins led to a sharp decrease of final conversion which could not be explained by the glass transition effect alone. They attributed this phenomenon to chain segmental immobility in a crosslinked network. Yang and Lee[4] investigated the effect of styrene concentration and the structure of polyester resins on the rheological and kinetic changes of polyester reactions. They found that gel conversions of unsaturated polyester resins were much higher than those predicted by the classical Flory–Stockmayer theory[5]. Many researchers[6–12] have mentioned similar findings for reactions of vinyl–divinyl systems. One reason for the deviation from the theory is the existence of extensive ring formation or intramolecular cyclization[11–17]. The delay in gel formation is explained by the competition between intermolecular (network formation) and intramolecular (cyclization) crosslinkings. Another explanation is that the reactivity of some C=C bonds of polyester molecules is reduced as the reaction proceeds[18,19]. As a result, the maximum network density is not reached. Minnema *et al.*[20] attributed this phenomenon to the molecular shielding of the pendant vinyl groups in the copolymerization process.

Dusek *et al.*[21] proposed that, for vinyl–divinyl systems with medium or high concentrations of divinyl monomers, compact 'microgel-like' particles can form during reaction, which may affect the reaction kinetics. Although many researchers[21–26] have found experimental evidence to support the formation of microgels in free-radical copolymerizations, very few studies have shown the size and shape of those particles[7]. In this work, a series of unsaturated polyester resins with differing chemical structure were studied by observing their morphology using scanning electron microscopy. The major goal is to investigate the structure of microgel particles in vinyl–polyvinylene systems such as unsaturated polyester resins.

EXPERIMENTAL

Materials

Three unsaturated polyester resins were provided by Ashland Chemical Co. These polyesters consist of maleic anhydride, isophthalic acid and propylene glycol with different molar ratios. Maleic anhydride provides vinyl groups to the polyester resin while propylene glycol and isophthalic acid serve as chain extenders. The aromatic ring structure of the isophthalic acid also makes the chain more rigid and more compatible with styrene monomer. The number-average molecular weights of these three resins are very close, ranging from 1580 to 1700, but the degree of unsaturation varies. The average number of vinylenes per molecule ranges from 6.56 to 10.13. The detailed compositions of the materials used in this study and the resin codes are given in *Table 1*. The resin codes, S-6, S-8 and S-10, correspond to the degree of unsaturation.

From *Table 1*, one may conclude that, among the three resins, the S-10 resin has the highest degree of unsaturation

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Table 1 Unsaturated polyester resins used in this study

	Unsaturated polyester resins		
	S-10	S-8	S-6
Composition (molar ratio)			
Maleic anhydride	1	4	2
Isophthalic acid	0	1	1
Propylene glycol	1	5	3
$\bar{M}_n$ (g mol^{-1})	1580	1663	1700
Unit MW/mole C=C (g mol^{-1})	156	207.5	259
Avg. no. of C=C/polyester molecule	10.13	8.01	6.56
$\bar{r}$ (Å)[a]	18.70	19.58	20.99

[a] Root-mean-square end-to-end distance[27]

and the most flexible chain. In addition, the S-10 resin is less compatible with styrene monomer. On the other hand, the S-6 resin has the lowest degree of unsaturation, has a more rigid chain and should be more compatible with styrene monomer.

All polyester resins and styrene monomer were used as received without removing the inhibitor. Methyl ethyl ketone peroxide (MEKP, Lucidol) with 25% cobalt naphthenate promoter, a room-temperature initiator, was used to initiate the reaction. The concentration of the initiator and promoter was 1% by weight of total resin for all samples. Before the experiment, the polyester resin was weighed and mixed with styrene monomer in a flask at the desired molar ratio. The mixture was mixed with a magnetic stirrer for 15–20 min in a 60°C water bath to dissolve the polyester resin in the styrene monomer. The prepared solution was stored at 5°C for further use. To start the measurement, the solution was mixed with the initiator and promoter at room temperature, and was then quickly sampled and loaded for kinetic and morphological measurements.

Instrumentation and procedure

For the morphological study, the resins prepared were moulded into a disc shape at 30°C in a sealed glass dish which was located in a constant-temperature water bath for 10 h.

After reaction, the moulded discs were broken into several pieces. One piece was etched in dichloromethane for more than 10 h to dissolve the soluble materials on the fracture surface. This piece was then dried at room temperature for 4 h and gold-coated for morphological measurement. A Hitachi S-510 scanning electron microscope with 25 keV power was used to view the fracture surface of each sample at magnifications from 800 × to 4000 ×.

The reaction kinetics of styrene monomer and polyester vinyl groups were measured by an *FT*i.r. spectrometer (Nicolet 20DX) with a resolution of 4 cm^{-1} in the transmission mode. The monomer conversion of each resin was measured by following the changes of its characteristic peaks. For the styrene–unsaturated polyester resins, the content of styrene monomer can be determined from the peaks at 912 and 992 cm^{-1}, while that of C=C bonds of unsaturated polyester resins can be determined from a peak at 982 cm^{-1}. The detailed experimental procedure, instrument calibration and data analysis were described in a previous work[28].

MECHANISM OF MICROGEL FORMATION

In the styrene (ST)-unsaturated polyester (PES) crosslinking copolymerization, there are three possible reactions: ST to ST, ST to PES C=C bond, and PES C=C bond to PES C=C bond. As shown in *Figure 1*, these reactions can be further classified into four types: (I) intermolecular crosslinking with or without linking through styrene monomers; (II) intramolecular crosslinking with or without linking through styrene monomers; (III) branching on the polyester molecule by styrene; and (IV) free styrene homopolymerization. Among the four, reaction (I) results in a macroscopic network formation through the connection of adjacent polyester molecules; reaction (II) increases the crosslinking density and reduces the size of polyester coil, but does not contribute to the macroscopic network formation; reaction (III) consumes crosslinking units and may slightly increase the polymer coil size, but has little effect on network formation; and reaction (IV) forms a soluble polymer segment which does not participate in the polymer network. Although all the reactions affect the curing kinetics, only the first two contribute to network formation.

During the ST/PES copolymerization, the initiator decomposes and creates free radicals in the system. The free radicals grow and form long-chain molecules through connecting styrene monomers and polyester molecules by both inter- and intramolecular reactions. The schematic of the growth of free radicals is shown in *Figure 2a*. These long-chain molecules tend to form a spherical type of structure or 'microgel particle' as shown in *Figure 2b*, due to the intramolecular crosslinking among the pendant C=C bonds of polyester molecules. In other words, the formation of microgel particles is based on the primary polymer chains through the intramolecular crosslinkings[21]. Experimental evidence[16,29,30] showed that the primary microgel particles form at very early stages of reaction.

Figure 2b shows that many pendant C=C bonds are buried in the core of the microgel particles. The buried

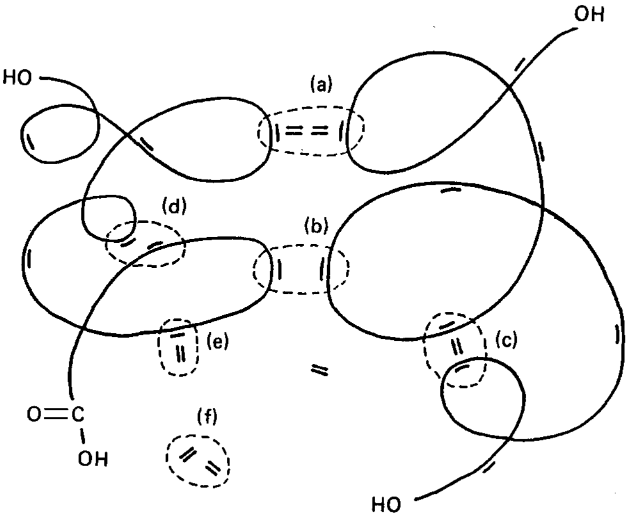

Figure 1 Schematic diagram showing all possible reactions in the styrene–unsaturated polyester copolymerization: I, intermolecular crosslinking, E–(S)$_n$–E′ (a) and E–E′ (b); II, intramolecular cyclization, E–(S)$_n$–E (c) and E–E (d); III, branching growth, E–(S)$_n$ (e); and IV, styrene homopolymerization, S–S (f)

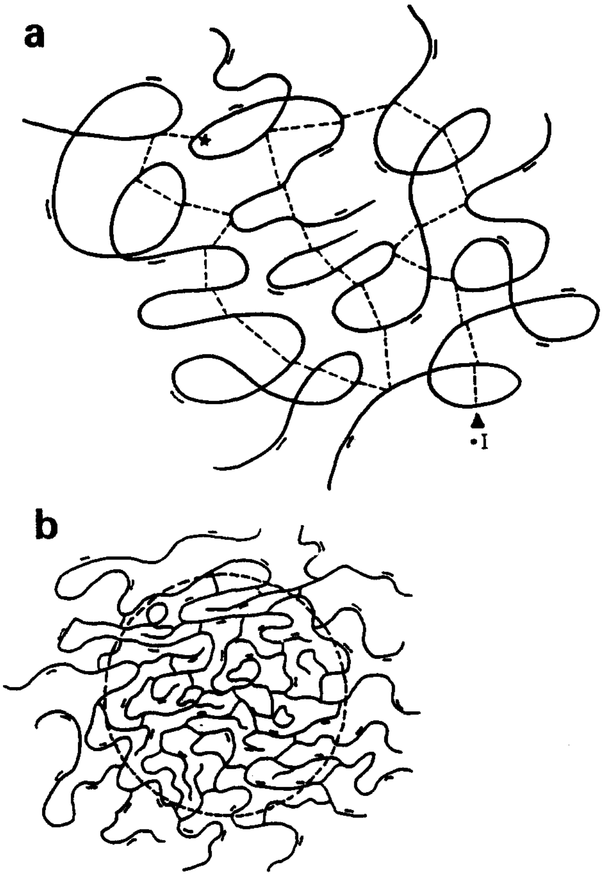

Figure 2 Formation of microgel particles through the growth of free radicals: (a) growth of free radicals; (b) formation of microgel particles[21]

pendant C=C bonds may react with diffusing-in styrene monomers through free radicals, which may further enhance the intraparticle crosslinking. This tends to reduce the size of the microgels and make them more compact. Finally, the compactness of the gel particle prevents the styrene monomers from diffusing into the particle core, and results in more unreacted pendant C=C bonds remaining in the microgel particle.

The interparticle crosslinking, forming macroscopic network structure, may occur through C=C bonds at or near the surface of the microgels with styrene monomers serving as chain extenders. Depending on the concentration of styrene monomers and microgels, the morphology of reacted resins can be quite different. *Figure 3* shows the possible morphological structures of reacted unsaturated polyester resins. At high styrene concentrations, i.e. low concentration of microgels, the individual microgel particle can be easily observed and the microgel size is large due to the styrene swelling effect. The particles are externally connected by styrene chains to form a 'dumbbell' shape with particles at the ends and styrene chains in the middle. The overall network built up by the dumbbell shape is a 'tree-like' or 'coral-like' structure as shown in *Figure 3a*.

In the case of low styrene concentration or high microgel content, the microgels are closely packed together. They tend to entangle and overlap with each other, so that no individual particle or dumbbell shape can be observed. The structure at a fracture surface is 'flake'-like as shown in *Figure 3c*.

Different from the two extreme cases, *Figure 3b* shows the structure at a medium concentration of microgels. Although the microgels tend to agglomerate and form a flake-type structure, some pores remain in the structure because there are not enough microgels to fill up the entire space. The size of flakes is also smaller in this case. Such a structure can be considered as a 'flake-and-pore' type.

In the following section, we shall present experimental results showing the above-mentioned morphological structures.

RESULTS AND DISCUSSION

Figure 4 shows the SEM micrographs of the fracture surfaces of the moulded ST/S-10 resins at different molar ratios (MR) of styrene to polyester C=C bonds; *Figure 5* shows the micrographs with higher magnification at elevated molar ratios. One can clearly observe the coral-like structure and the dumbbell shape connection in *Figures 4a, 4b* and *5* at high molar ratios (i.e. $MR = 3/1$ and 4/1), which corresponds to the case shown in *Figure*

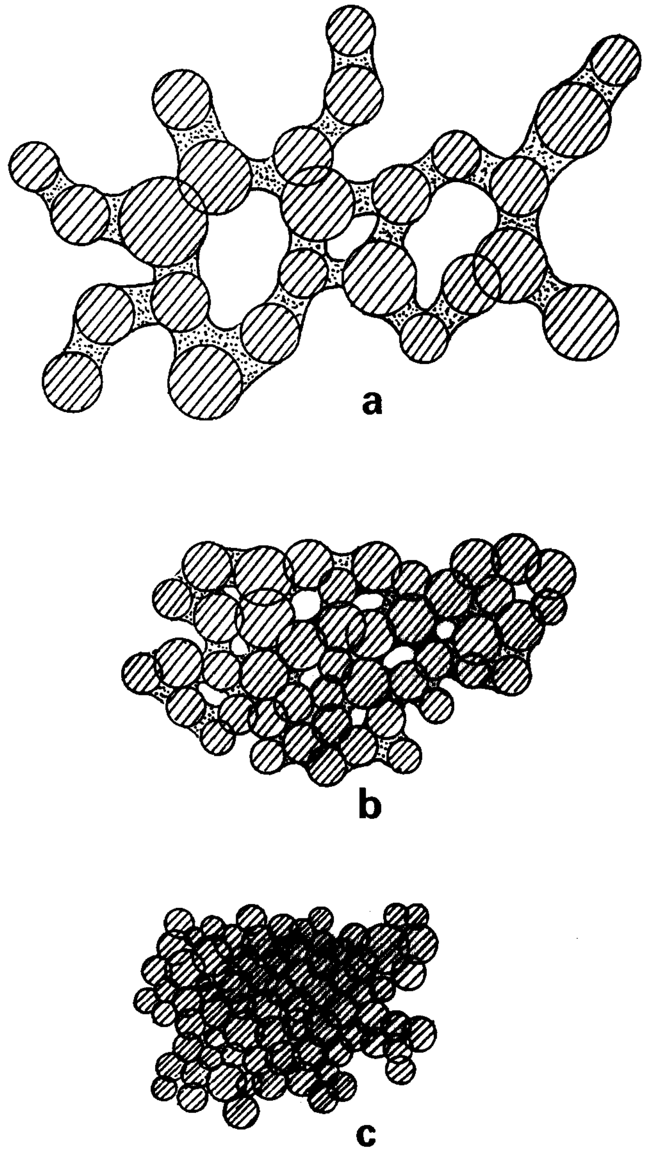

Figure 3 Structures of polyester resins based on microgel formation: (a) coral-like structure with dumbbell shape and interparticle connection; (b) flake-and-pore structure; and (c) flake-type structure

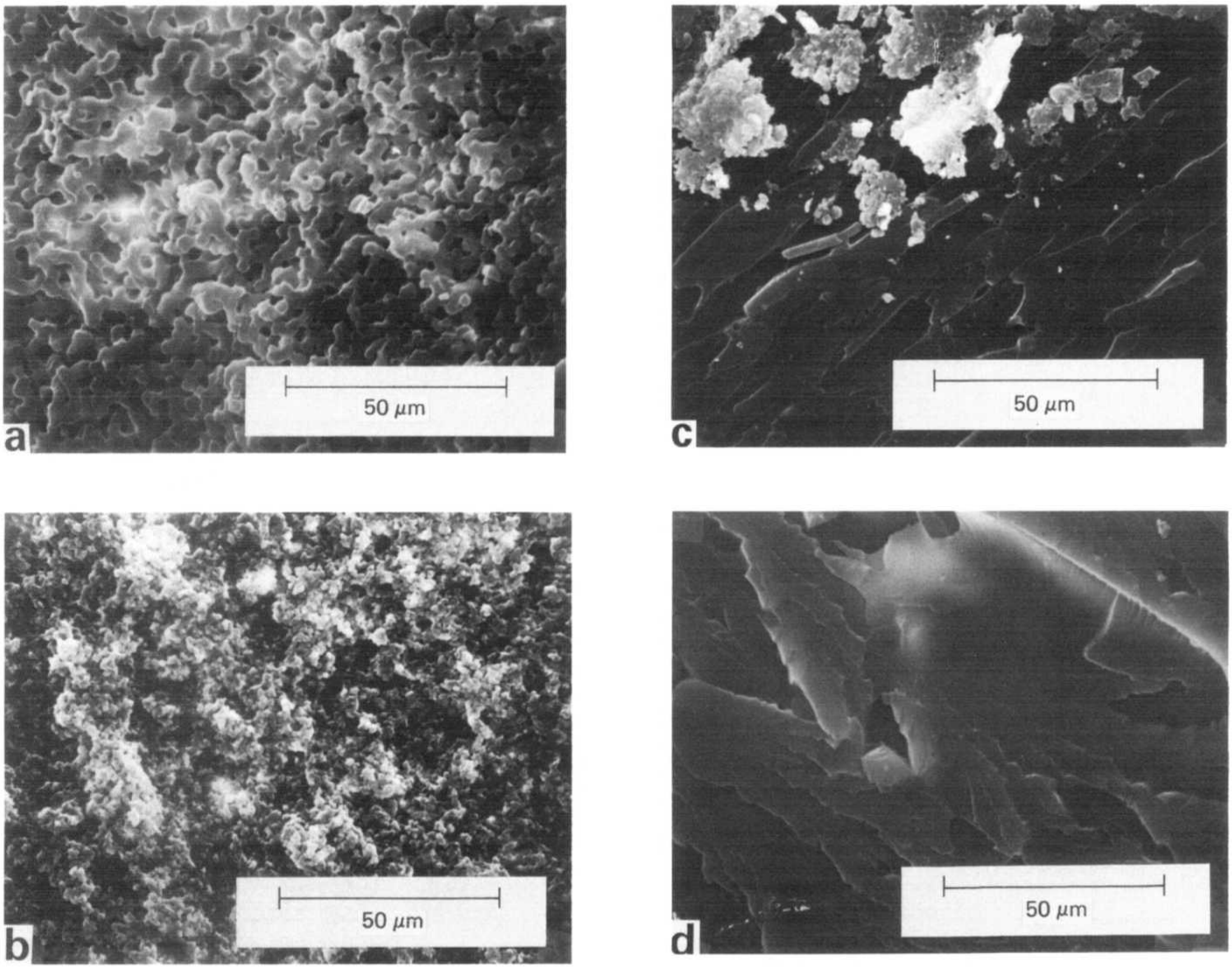

Figure 4 SEM micrographs of ST/S-10 samples with $MR=4/1$ (a), 3/1 (b), 2/1 (c) and 1/1 (d)

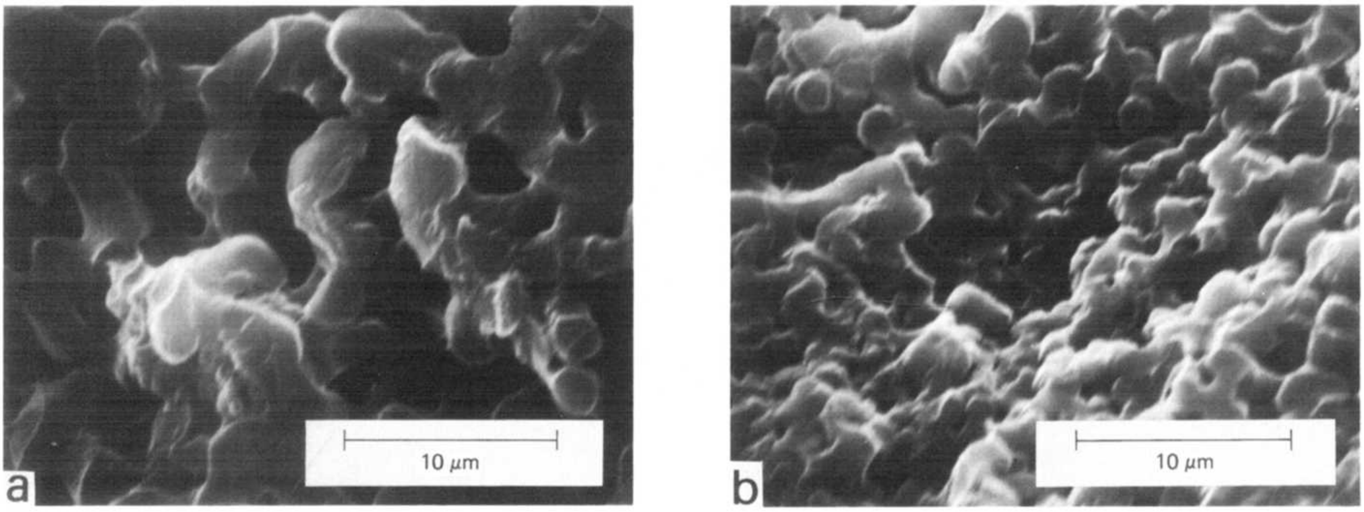

Figure 5 SEM micrographs of ST/S-10 samples with $MR=4/1$ (a) and 3/1 (b) at high magnification

3a. On the other hand, *Figure 4d* shows a flake-type structure for the system with $MR=1/1$ (i.e. low styrene concentration and high microgel content). The system with $MR=2/1$ results in a flake-and-pore type structure as shown in *Figure 4c*. Comparing *Figures 4c* and *4d*, one can see that the flake size of the former is smaller than that of the latter. This is because the microgels in the latter case are more entangled and overlapped with each other due to the higher concentration of microgels.

Figure 5 compares the microgel structure of resins at higher magnification. It reveals that higher styrene dilution increases the chance for the formation of

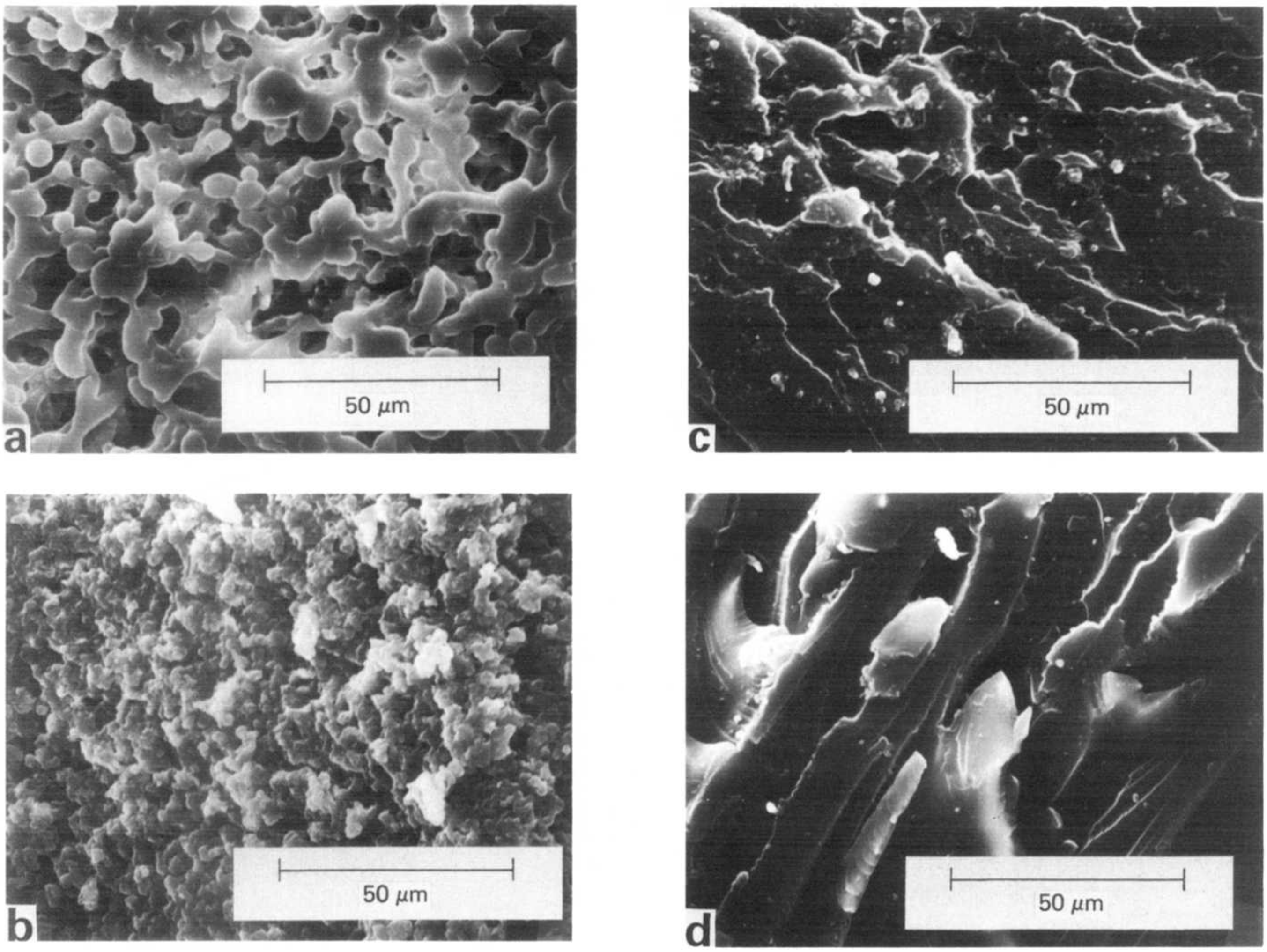

Figure 6 SEM micrographs of ST/S-8 samples with $MR=6.67/1$ (a), 4/1 (b), 2.66/1 (c) and 2/1 (d)

individual microgel particles and enhances the dumbbell type interparticle connection. Quantitatively, the system with $MR=3/1$ shows an average particle size around 1.84 μm. On the other hand, the more diluted system with $MR=4/1$ shows a larger average particle size, around 2.63 μm, because of the styrene swelling effect.

The SEM micrographs of the fracture surfaces of the moulded ST/S-8 resins are shown in *Figure 6*. The systems with $MR=2/1$ form a small flake structure (*Figure 6d*), while the system with $MR=2.66/1$ shows a flake-and-pore structure (*Figure 6c*). In contrast, the systems with higher MR, $MR=6.67/1$ and 4/1, exhibit a coral-like structure (*Figures 6b* and *6a*). These structures are similar to those shown in *Figure 4*. *Figure 7* clearly shows the coral-like structure of samples with $MR=4/1$ and 6.67/1. The average particle sizes are around 3.16 μm for $MR=4/1$ and 6.32 μm for $MR=6.67/1$.

Similarly, for the moulded ST/S-6 resins, *Figure 8* shows a flake-type structure for $MR=2/1$ (*Figure 8d*), a flake-and-pore structure for $MR=3.32/1$ (*Figure 8c*) and coral-like structures for $MR=4/1$ and 6.67/1 (*Figures 8b* and *8a*). The enlargement of the coral-like structures of *Figures 8a* and *8b* is shown in *Figure 9*. The average particle sizes are around 3.95 μm and 10.53 μm for $MR=4/1$ and $MR=6.67/1$, respectively.

Table 2 summarizes the average particle sizes of visible microgels for samples moulded at 30°C. Several observations can be pointed out. First, each microgel particle consists of several hundreds or more polyester molecules because the microgel particles have measured sizes of the order of several micrometres, while the coil size of a single polyester molecule is less than 100 Å (refs. 27 and 31). Secondly, for each polyester resin, increasing the molar ratio of styrene to PES C=C bonds increases the microgel size due to the styrene swelling effect. Thirdly, at $MR=4/1$, the microgel size of the unsaturated polyester resins range from 2.63 μm for ST/S-10, to 3.16 μm for ST/S-8 and 3.95 μm for ST/S-6 resin (i.e. *Figures 5a, 7b* and *9b*, respectively). This is probably because S-6 and S-8 resins contain stiff benzene rings in the polyester chain, which results in a larger polymer coil and, consequently, a larger microgel particle. Another reason is that the benzene structure of S-6 and S-8 resins makes them more compatible with styrene monomers; therefore, more styrene can diffuse into the microgels and result in larger particles. Furthermore, the higher degree of unsaturation of S-10 resin increases the chance of intraparticle crosslinkings, which may make these gel particles more compact. The particle size of S-6 resin is larger than that of S-8 resin because the former possesses more benzene structure. The difference of microgel particle size is even greater when comparing samples at constant weight ratio (WR) of styrene to unsaturated polyester. At $WR=2.67/1$, the microgel sizes are 2.63, 4.21 and 10.53 μm for ST/S-10, ST/S-8 and ST/S-6 resins, respectively.

Samples with $MR=2/1$ are of particular interest

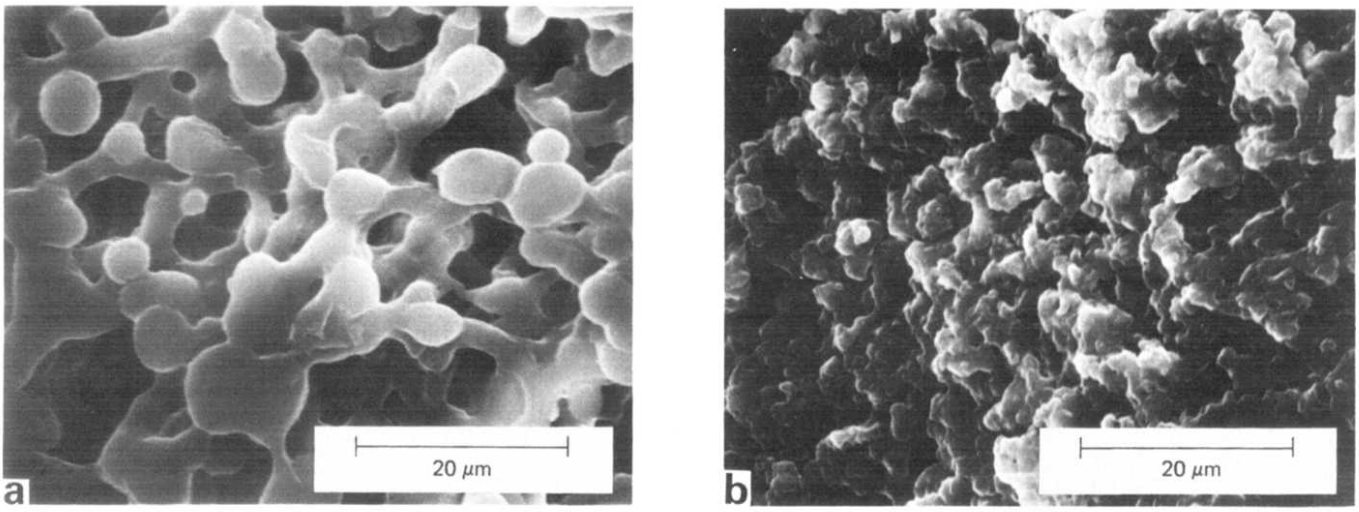

Figure 7 SEM micrographs of ST/S-8 samples with $MR = 6.67/1$ (a) and 4/1 (b) at high magnification

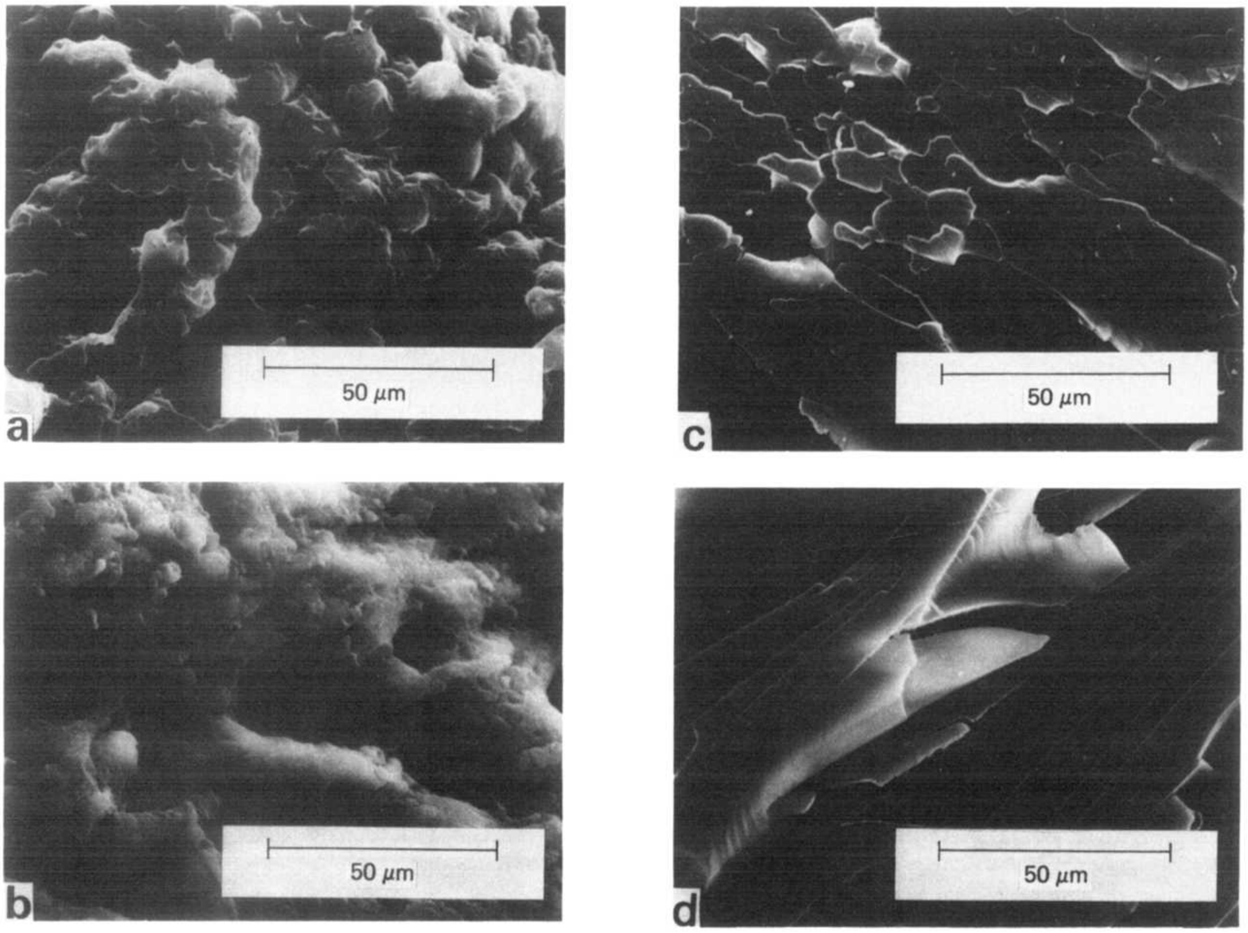

Figure 8 SEM micrographs of ST/S-6 samples with $MR = 6.67/1$ (a), 4/1 (b), 3.32/1 (c) and 2/1 (d)

because most commercial ST/PES resins used in sheet moulding compounds have this combination. Comparing *Figures 4c, 6d* and *8d*, one can see that the fracture structure changes from a flake-and-pore type for ST/S-10 resin to a large flake type for ST/S-6 resin. This is because ST/S-6 resin has a lower *WR* (i.e. more unsaturated polyester molecules in a unit volume of resin) than the other two resins. In addition, the individual microgel size of ST/S-6 resin is larger than that of the other two resins at the same *MR*, which enhances the chances of chain entanglement among the microgels of ST/S-6 resin.

All the resins discussed above were moulded at 30°C. Their monomers were not completely reacted and the conversions were relatively low due to the low reaction temperature. For instance, *F*T*i.r.* measurement indicated that the ST/S-10 resin with $MR = 4/1$ only reached 34% styrene conversion, 90% PES C=C conversion and 44% overall C=C conversion after 8 h of reaction. The large

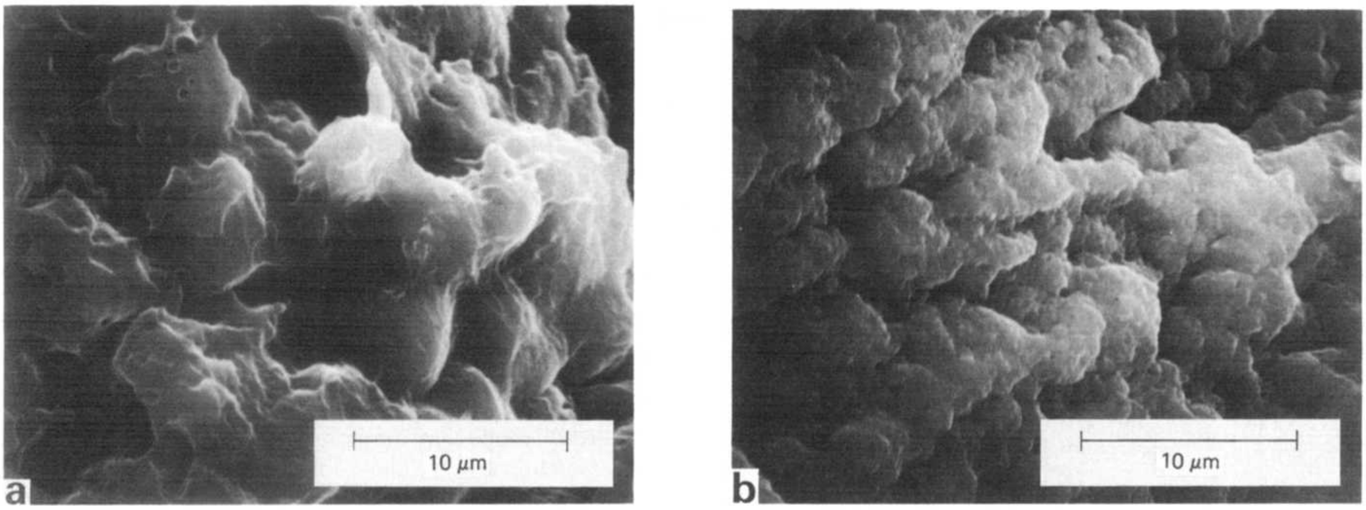

Figure 9 SEM micrographs of ST/S-6 samples with $MR=6.67/1$ (a) and 4/1 (b) at high magnification

Table 2 Comparison of microgel particles of unsaturated polyester resins

Resins	*MR*	*WR*	Avg. microgel size (μm)
ST/S-10	3/1	2/1	1.84
	4/1	2.67/1	2.63
ST/S-8	4/1	2/1	3.16
	5.33/1	2.67/1	4.21
	6.67/1	3.33/1	6.32
ST/S-6	4/1	1.5/1	3.95
	5/1	1.88/1	5.53
	6.67/1	2.67/1	10.53

portion of the pore space shown in *Figures 4a* and *6a* is attributed to the unreacted monomers and free polystyrene and polyester chains which have been removed by dichloromethane treatment before SEM measurement.

To study the post-curing effect, an untreated, 30°C cured sample of ST/S-10 resin with $MR=4/1$ was put in an oven at 200°C for 1 h before SEM measurement. The final conversions are over 96% for both styrene and PES C=C bonds. The SEM result is shown in *Figure 10*. Most of the pore space has been filled up by the reaction of residual styrene monomers which must be attached to the network structure because they could not be removed by dichloromethane treatment. The pores shown in *Figure 10* are the result of styrene evaporation during the post-curing process.

Table 3 lists the final conversions of styrene, polyester C=C bonds and overall C=C bonds determined by *FT*i.r. for samples reacted at 30°C for 8 h. Apparently, all samples show incomplete reaction. At low *MR* the styrene conversion is higher than that of polyester C=C bonds, while at high *MR* the trend is reversed. This trend seems to follow the change of sample morphology. At high *MR*, the unsaturated polyester resins tend to form individual microgel particles. Most polyester C=C bonds are located inside these particles and can react easily because of a high local concentration. The reaction may be through the linkage of trapped or diffusing-in styrene monomers. Most styrene monomers, however, are located outside the microgel particles and have to be reacted by styrene homopolymerization. Since styrene–polyester vinylene reaction is more favourable than styrene–styrene reaction[1,32], the moulded sample shows a high α_E (PES C=C conversion) and low α_S (styrene conversion). On the other hand, the morphology of moulded samples at low *MR* reveals a flake-type structure, which implies that most polyester chains are entangled with each other and

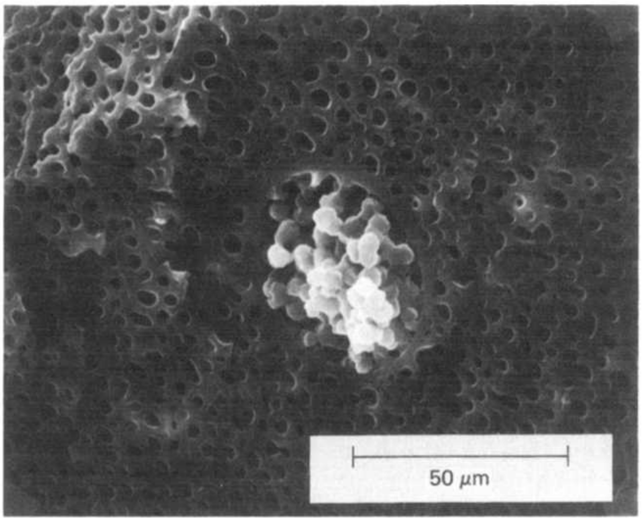

Figure 10 SEM micrographs of ST/S-10 samples with $MR=4/1$ after post-cure

Table 3 Measured conversion of unsaturated polyester resins at 30°C by *FT*i.r. for various *MR* from 1/1 to 4/1

	ST/S-10				
	1/1	1.5/1	2/1	3/1	4/1
α_S[a]	0.66	0.74	0.65	0.49	0.34
α_E[b]	0.58	0.67	0.85	0.87	0.90
α_T[c]	0.62	0.71	0.72	0.59	0.44
	ST/S-8			ST/S-6	
	1.5/1	2/1	2.66/1	2/1	3.32/1
α_S	0.71	0.69	0.77	0.70	0.76
α_E	0.57	0.80	0.85	0.60	0.89
α_T	0.65	0.73	0.79	0.67	0.80

[a] Styrene conversion
[b] Polyester C=C conversion
[c] Overall C=C conversion

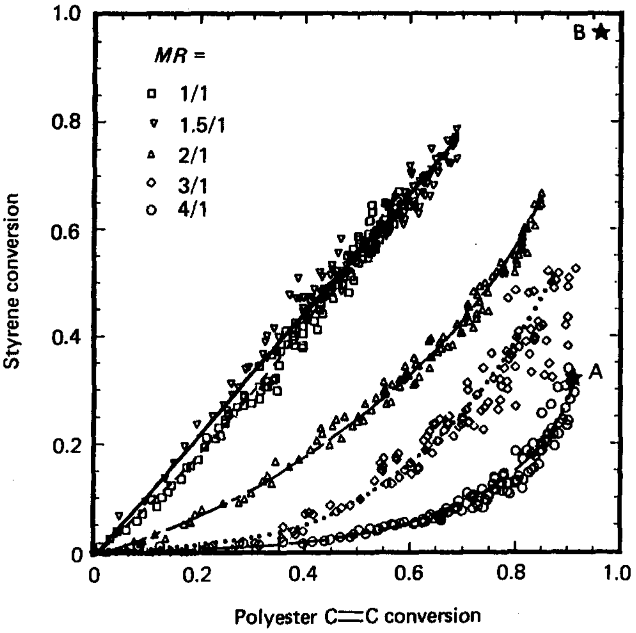

Figure 11 Styrene conversion (α_S) vs. polyester C=C conversion (α_E) for reactions of ST/S-10 resins at 30°C measured by *FT*i.r.: point A, before post-cure; point B, after post-cure

are better mixed with styrene monomers. Since styrene is more mobile than the entangled polyester chains, the final conversion of styrene is higher than that of polyester C=C bonds. The transition seems to occur when the sample structure changes from flake type to flake-and-pore type. For instance, at $MR = 2/1$, both ST/S – 10 and ST/S-8 reaction show higher α_E and lower α_S. The SEM photographs in *Figures 4c* and *6d* reveal a flake-and-pore type structure for these two samples. On the other hand, ST/S-6 reaction shows a lower α_E and higher α_S. Examining the SEM photograph in *Figure 4d*, this sample reveals a large flake structure.

Figure 11 plots styrene conversion vs. PES C=C conversion for ST/S-10 resin. All reactions show up-bending curves. As the *MR* increased from 1/1, 2/1, 3/1 to 4/1, the curves tend to shift downwards, which indicates that, at the same styrene conversion, more PES C=C bonds have been consumed in a more diluted system (i.e. higher *MR*). For $MR = 3/1$ and 4/1, there is very low styrene consumption until the PES C=C conversion reaches 40%. This is because of the formation of microgel particles as explained before. For the cases of $MR = 1.5/1$ and 1/1, the relative conversion curves are very close to each other with a slightly higher styrene conversion than polyester C=C conversion. The same morphology, flake-type structure, may have caused this similar reaction path for the two samples.

Also shown in *Figure 11* are the final conversions of ST/S-10 resin with $MR = 4/1$ before and after post-cure at 200°C for 1 h (i.e. points A and B). Post-cure greatly increased the styrene conversion, but only slightly improved the PES C=C conversion. Similar results were found for all other samples. For instance, the ST/S-6 resin with $MR = 2/1$ represent a system with flake-type structure. Before post-cure, the resin has 70%, 60% and 67% conversions for styrene, PES C=C bonds and overall C=C bonds, respectively. Post-cure changed these conversions to 95%, 73% and 88%. Again, styrene conversion is largely improved but PES C=C conversion shows only a moderate change. It appears that many polyester pendant C=C bonds are trapped in the highly crosslinked network structure and remain unreacted even at high temperatures.

CONCLUSIONS

The formation of microgel particles is a key feature of the styrene–unsaturated polyester copolymerization. The network structure can be coral-like or flake-like depending on the concentration and type of polyester resins in the reacting system. Formation of microgels enhances the intraparticle crosslinkings, which causes a fast consumption of PES C=C bonds at early reaction and the delay of system gelation. Many pendant polyester C=C bonds may be trapped in the compact microgels and become permanent residue. The *FT*i.r. spectroscopic method can measure both styrene and polyester C=C conversions. The measured copolymerization kinetics agree well with the concept of microgel formation and can be explained by the observed polymer morphology.

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