Cross-Linking Self-Emulsifying Copolymerization of an Unsaturated Polyester and Styrene

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ABSTRACT: Reactive microgels (RMs) were synthesized by a self-emulsifying copolymerization of an unsaturated polyester (UP) and styrene (St) with azobis(isobutyronitrile) (AIBN) as initiator. The influence of UP/St mass ratio on copolymerization rate, composition, molar mass (M_w), particle diameter (d_z), intrinsic viscosity ([η]), polydispersity index (M_w/M_n), and glass transition temperature (T_g) of RMs has been investigated. In agreement with an earlier experiment where an electrolyte (KCl) was added to the reaction mixture, the composition of the RM did not change with increasing conversion. It must be concluded therefore that the presence of this electrolyte has no influence on the composition of the RM. The constant composition implies that practically no diffusion of the reaction components to growing RM particles takes place during the copolymerization.

Introduction

Reactive microgels (RMs) are small particles, have a low viscosity in solution, and can react with other chemical groups.[1−3] They may be used as photosensitive polymers in photopolymerization,[4] in thermosensitive polymers for ion adsorption,[5] as cross-linking agents for interpenetrating networks,[6,7] and as substrates for biochemical purposes.[8]

The preparation of RMs by emulsion copolymerization (ECP) of unsaturated polyester (UP) with terminal carboxylic acid groups and styrene is of special interest, because these systems are self-emulsifying and may form microemulsions without needing another external emulsifier. Kolitz et al.[9] studied the ECP of UP and styrene, using potassium peroxydisulfate ($K_2S_2O_8$) as initiator and poly(oxyethylene) nonyl phenyl ether as emulsifier, and varied the UP/styrene ratio. They found that the compositions of the RMs were different from those in the original mixtures of both components. In a later study of the influence of electrolyte on the copolymerization of UP and styrene in a microemulsion, the final composition of the RM was independent of the amount of the added electrolyte, KCl.[10] This result was surprising because it implied that during the copolymerization either no diffusion of the reacting components in the aqueous phase took place or both components had the same diffusion rate. Considering the different size and water solubilities of the UP and styrene, the latter possibility was questionable. However, because the conversion of UP and styrene to RM was almost quantitative, the sheer independence of the composition from the concentration of the electrolyte did not allow conclusions about the mechanism of this ECP.

In further experiments,[11] the composition of RM was determined after different conversions or reaction times. It turned out that again the composition remained constant and equal to that of the original mixture. The present study should reveal whether the presence of the electrolyte, KCl, was responsible for the constant composition of the RM. Therefore, RMs were synthesized under the same conditions as in the previous study but without an electrolyte. Meanwhile, because the UP is not only a reactive component but also acts as emulsifier for styrene in the emulsion copolymerization, it was examined how the UP/St mass ratio influences the self-emulsifying copolymerization of these components. For this purpose, except for the UP/St mass ratio 80/20 employed in the preceding study, two other mass ratios with a higher mass fraction of styrene (70/30 and 60/40) were chosen to synthesize RM.

Experimental Section

Materials. 1,6-Hexanediol (Merck, pro synth.), maleic anhydride (Merck, pro synth.), NaOH (Merck, p.a.), HCl (36% in water, Merck), and azobis(isobutyronitrile) (AIBN, Merck, p.a.) were used without further purification. Acetone (Merck, p.a.), dioxane (Merck, p.a.), and tetrahydrofuran (Merck, p.a.) were distilled before use. Water was distilled under nitrogen. Styrene (St, Merck, p.a. or 99%, Aldrich) was washed with a 5% aqueous solution of KOH (or 5% aqueous solution of NaOH) to remove the inhibitor and then 4 times with water, dried over anhydrous sodium sulfate, and distilled under reduced pressure.

Preparation of the Unsaturated Polyester. The unsaturated polyester was synthesized by melt condensation. 1,6-Hexanediol (2.0 mol) and maleic anhydride (2.3 mol) were mixed in a 1 L glass vessel and heated to 100 °C with stirring. The mixture was stirred at 100 °C for 24 h, at 130 °C for 3 h, and at 150 °C for another 15 h, cooled to 100 °C, and kept at this temperature for 21 h. Maleic anhydride (0.2 mol) was added to transform all terminal hydroxyl groups of the UP into carboxylic acid groups. After cooling to room temperature, a colorless UP of low viscosity was obtained, which was dissolved in acetone and fractionated by adding water. The UP fractions were dried under vacuum for 24 h. The mean molar mass (M_n) of the UP was determined by titration of the carboxylic acid groups with phenolphthalein as indicator. For this study, an UP with a mean molar mass (M_n) of 1100 was used. The degree of isomerization was measured by ^{1}H-NMR with $CDCl_3$ as internal standard. The characteristic peaks for maleic and fumaric acid units at 6.3 and 6.9 ppm were used for analysis. The UP contained 28% maleic units, in agreement with an analysis by mass spectroscopy.[12]

Preparation of Reactive Microgels. Reactive microgels were prepared from the UP and styrene by self-ECP. The composition of self-ECP used in this study is listed in Table 1. A typical procedure of self-ECP is as follows: 100 mL of water was added by a syringe to a 200 mL water-jacketted reaction vessel under nitrogen. Then 3.2 g of the UP was dispersed in the water at 70 °C under stirring and neutralized

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Table 1. Composition of Self-Emulsifying Copolymerization[a]

UP/St (mass ratio)	UP (g)	St (g)	NaOH (0.4 N) (mL)	water (mL)	AIBN (g)
80/20	3.2	0.8	10	100	0.1
70/30	2.8	1.2	8.7	100	0.1
60/40	2.4	1.6	7.2	100	0.1

[a] Copolymerization temperature: 70 °C.

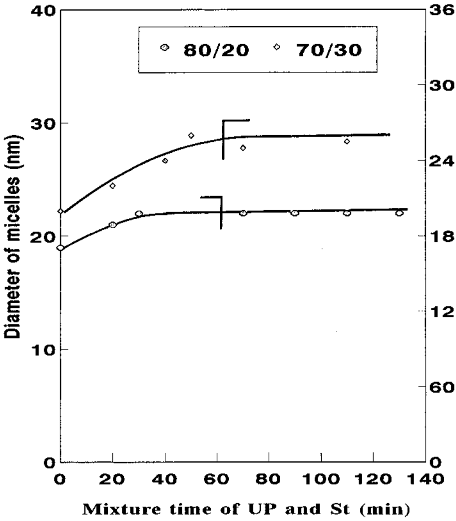


Figure 1. Effect of the mixing time on the diameter of micelles.

with 10 mL of aqueous NaOH (0.4 N). After 15 min, 0.8 g of St was added and solubilized for 3 h. The copolymerization was started with 0.1 g of AIBN, which was dissolved in a small amount of acetone. The reaction temperature was 70 °C. The copolymerization was terminated by cooling the reaction vessel with an ice bath and adding 100 mg of hydroquinone. The RMs were precipitated by 5 mL of HCl (2 N), filtered, and washed with 1.5 L water until free of chloride ions. To determine the unreacted amount of styrene, the RMs were dispersed in toluene and filtered, and the filtrate was analyzed for styrene by gas chromatography.

Characterization of Reactive Microgels. The compositions of the RMs were measured by elemental analysis.

The molar mass (M_n) of the RM was determined by light scattering with dioxane as solvent. A KMX-6 low-angle light scattering photometer and a KMX-16 laser differential refractometer were used to measure the Rayleigh ratio and the refractive index increment (dn/dc).

The mean hydrodynamic diameters (d_z) of the micelles and the particle diameters of the RMs in dioxane were measured by dynamic light scattering at 20 °C.

The glass transition temperatures (T_g) of the RMs were measured with a differential scanning calorimeter (DSC) (Perkin-Elmer). The rate of temperature increase was 10 °C/min.

The intrinsic viscosities [η] were determined with an automatic Ubbelohde viscometer in dioxane at 20 °C.

The polydispersity indices of the RMs (M_w/M_n) were obtained by gel permeation chromatography (GPC) (Waters 440) in tetrahydrofuran with a flow rate of 1.0 mL/min. GPC columns were calibrated by a series of polystyrenes with narrow molar mass distributions and known molar masses, using tetrahydrofuran as elution solvent at room temperature.

Results and Discussion

Diameter of Micelles and of the Reactive Microgels. In the case of UP/St ratio 80/20, the diameter of the UP micelles was about 19 nm, increased on the addition of styrene to 22.7 nm, and remained constant up to a mixing time of 70 min (Figure 1). Compared with a previous study,[11] the amount of styrene dissolved in the UP micelles was much higher in the presence than in the absence of an electrolyte, because the salt increases the lipophilicity of anionic surfactants[13] and accordingly also the micelle diameter. After the solubilization at the begining of the reaction, the mixture had a bluish and translucent appearance, which is typical for a microemulsion.[14] Contrary to the bluish, translucent 80/20 UP/St mixture, the appearance of the 70/30 and 60/40 mixtures was milky and opaque with a higher intensity at the larger fraction of styrene. This indicates that above about 20% of St, the microemulsion changed to a coarser emulsion. Correspondingly, the micelle diameter increased with the fraction of St from about 22 nm in case of the 80/20 mixture to about 250 nm in case of the 70/30 mixture (Figure 1). With the 60/40 mixture, the diameter of the micelles was too large to be measured by dynamic light scattering.

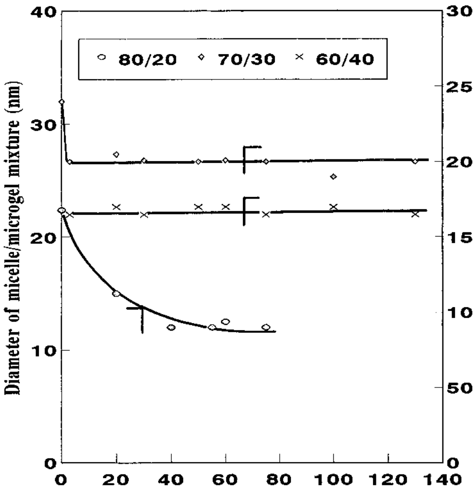


Figure 2. Effect of copolymerization time on the diameter of reactive microgels.

After about 50 min of mixing, the diameter of the micelles of the 70/30 mixture remained constant, i.e. somewhat later than in the case of the 80/20 mixture. The strong dependence of the micelle diameter on the UP/St mass ratio raises the question whether the large-sized species may still be considered as micelles or whether there is a continuous transition from micelles to monomer droplets.

Due to the volume contraction by the copolymerization and the intramolecular cross-linking, the diameter of the RMs initially decreased (see Figure 2). If the particle diameter was measured at different reaction times without distinguishing not yet reacted micelles from already formed RMs, the diameters again remained constant throughout the whole reaction time with about 12 nm for the 80/20 UP/St ratio and 200 and 170 nm for the 70/30 and 60/40 UP/St ratios, respectively. It is clear that the diameters of the RMs formed in the microemulsion are much lower than those formed in the coarser emulsion. The smaller diameter in the case of the 60/40 ratio is probably caused by a stronger contraction due to the higher fraction of styrene in the micelles. The initial decrease of the diameter from about 22 to about 12 nm for the 80/20 ratio and about 240 to about 200 nm for the 70/30 ratio indicates that a microgel particle forms very rapidly and does not grow significantly further during the copolymerization. On the other hand, the diameter of the RM formed in the presence of electrolyte was larger than that of the initially formed RM, probably due to an agglomeration.[11]

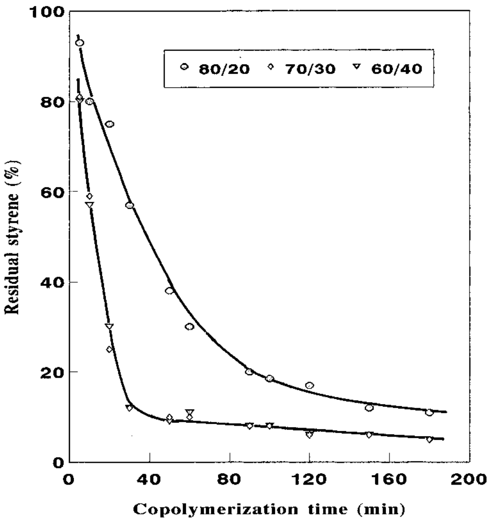


Figure 3. Conversion of styrene.

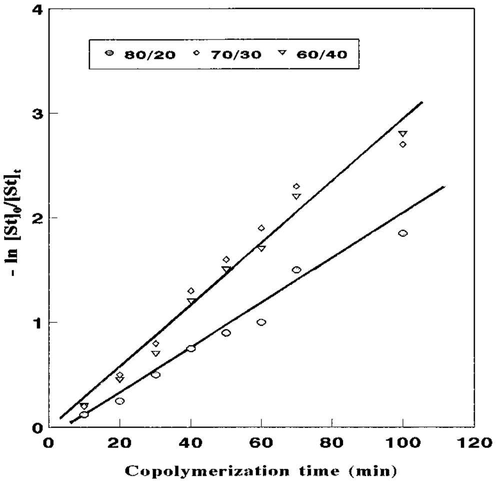


Figure 4. $-\ln[St]_0/[St]_t$ vs copolymerization time.

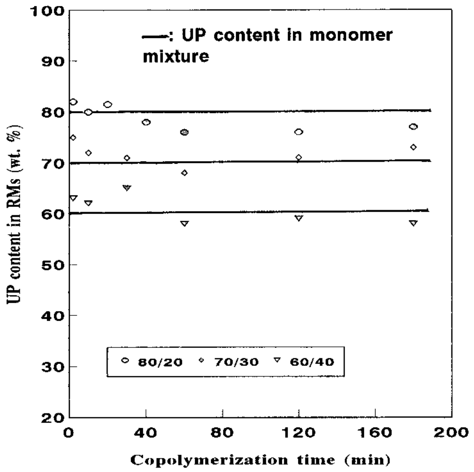


Figure 5. UP content of the RM during the copolymerization.

Table 2. Compositions of Different Fractions of RMs[a]

copolym time (min)	St units of the unfrac sample (wt %)	St units in the first frac of RM (wt %)	St units in the second frac of RM (wt %)
5	30.0	29.5	30.2
30	31.2	30.0	29.5
180	31.0	30.4	36.0

[a] Initial monomer mixture: UP/styrene = 70/30 (mass ratio).

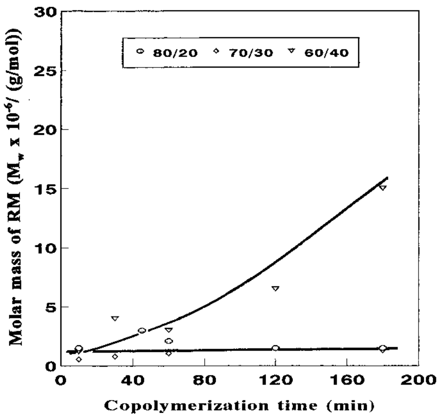


Figure 6. Molar mass of the RM during the copolymerization.

Obviously, the RMs formed in the absence of an electrolyte are much more stable, because no insoluble products appeared over the whole time of the reaction.

Copolymerization Rate. The copolymerization rate was measured by determining the conversion of styrene during the copolymerization. In the case of the 70/30 and 60/40 UP/St ratios, the rates were the same, but higher than that of the 80/20 ratio (Figure 3). Likewise, the apparent rate constant (k_p) for the mixtures with the larger fractions of styrene were higher than for that with the lower styrene fraction (Figure 4). The increased copolymerization rate may be due to the higher reactivity of styrene compared with the unsaturated units of the UP.[15] That the increase of the rate with the styrene fraction is not continuous may be attributed to the change from a microemulsion to a coarser emulsion.

Composition of the Reactive Microgels. The composition of the RMs, which were isolated after different reaction times, was determined by elemental analysis. As Figure 5 shows, the composition of the RMs was almost same as that of the initial reaction mixture and did not change during the copolymerization in the cases of three different UP/St ratios. This is also true for fractionated samples of RM (Table 2). The slightly increased styrene fraction of the second fraction (UP/St = 70/30) after a reaction time of 180 min may possibly be an error. From this result, it must be concluded that no diffusion of monomers, especially of styrene, to the growing particles takes place, irrespective of the change of a microemulsion to a coarser emulsion. This result also indicates that the mechanism of the copolymerization studied in this paper is different from normal emulsion copolymerization (EPC).[16] In a normal ECP, the monomers needed for the growth of the polymer particles are supplied by diffusion from the monomer droplets through the aqueous phase.

Molar Mass and Intrinsic Viscosity of the Reactive Microgels. Whereas the molar mass (M_w) of the RM with the lower fraction of St (St $\leq$ 30%) remained constant during the whole copolymerization, the M_w of the RM prepared with the higher fraction of styrene increased (Figure 6). Therefore, the copolymerization in a micelle with lower fraction of styrene must be a rapid process as compared with the whole reaction time, and the growth by diffusion of monomers from uninitiated micelles to polymerizing particles is negligible. The increase of M_w for the case of higher fraction of St was attributed to the onset of an aggregation of primary RM particles. This is also consistent with the increase of viscosity observed for the RM with the higher St fraction (see Figure 7). The decrease of $[\eta]$ during the copolym-

Table 3. Diameters of RMs (nm)

	UP/St (mass ratio)								
	80/20			70/30			60/40		
reacn time (min)	unfrac sample	first frac	second frac	unfrac sample	first frac	second frac	unfrac sample	first frac	second frac
5				22	19	16	60	56	38
10		48	24	19	17	11	53	45	31
30		41	18	17	17	10	51	40	33
60		29	20	23	11	10	61	53	41
120		24	13						
180		23	15	52	33	34	76	60	41

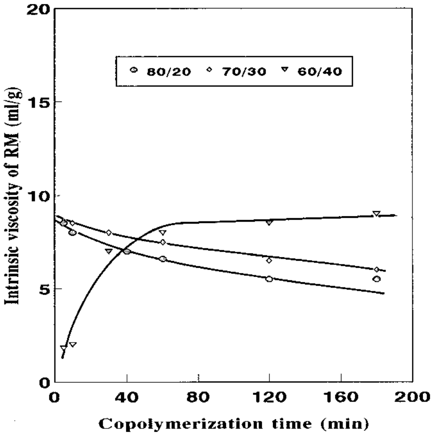


Figure 7. Intrinsic viscosity of RM isolated during the copolymerization.

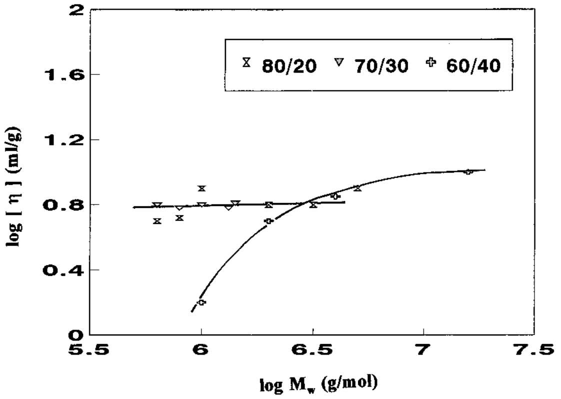
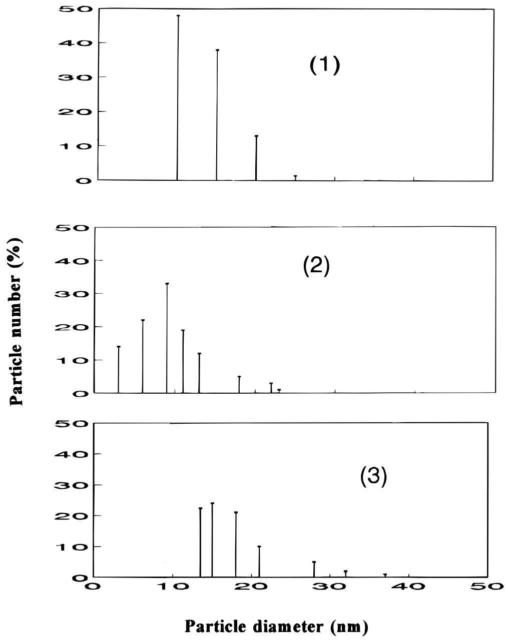
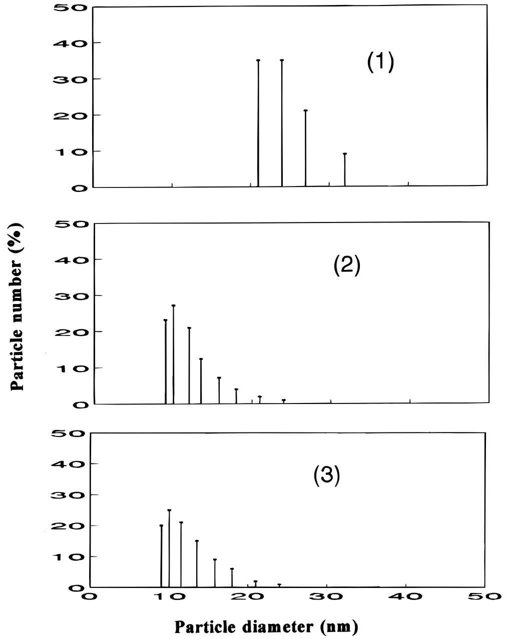


Figure 8. Relationship between log(intrinsic viscosity) and log(molar mass) of RM.

erization with lower fraction styrene is due to the intramolecular cross-linking, which continues over a much longer time than needed for the incorporation of the monomers in a micelle into the RM network. [η] of the RM was about 10 mL/g, and [η] of the UP only 5.9 mL/g. However, the molar mass of the RM was 1000 times larger than that of the UP. This difference indicates how much more compact the structure of RM is. The fact that for the case of lower fraction styrene, log[η] is independent of log(molar mass) of the RMs (see Figure 8) confirms the compactness of their structure.[17]



(a) 10 min



(b) 180 min

Figure 9. Particle size distribution of RM after a reaction time of (a) 10 and (b) 180 min. (The numbers 1, 2, and 3 indicate the fractions of the RM.)

Particle Diameter, Diameter Distribution, and Polydispersity of Reactive Microgels. In the microemulsion process, the mean hydrodynamic diameter (d_z) of the RMs decreased with increasing reaction time (Table 3). Later RM fractions, isolated by fractional precipitation, had a smaller size. In the coarser emulsion process, as to be expected, the RMs with the larger fraction of styrene also have the larger particle size, and due to an aggregation of the RM, the particle size increased toward the end of the copolymerization. The RMs isolated shortly after the copolymerization started were larger sized and had broader size distributions (Figure 9) than those isolated at the end of the reaction. This result indicates that the initial structure of the RM is not very uniform, but becomes more uniform during

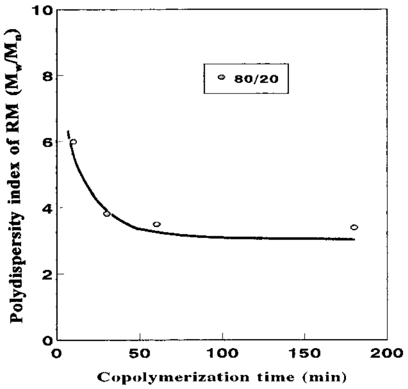


Figure 10. Polydispersity index of the RM during the copolymerization.

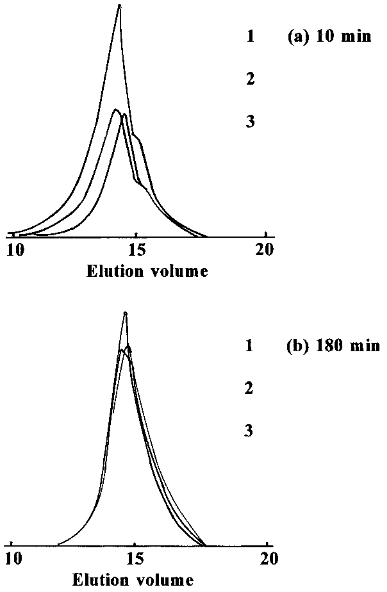


Figure 11. Profiles of gel permeation chromatography of RM isolated after (a) 10 and (b) 180 min. (The numbers 1, 2, and 3 indicate the fractions of the RM.)

Table 4. Glass Transition Temperature (T_g/°C) of RMs

UP/St (mass ratio)	copolym time (min) 10	180
80/20	101	130
70/30	120	130
60/40	135	155

the reaction due to the compacting effect of intramolecular cross-linking.

As to be expected from above results, the polydispersity (M_w/M_n) of the RM decreased during the reaction (Figure 10). Initially, the peak of the GPC diagram showed a shoulder (Figure 11a), which disappeared later on (Figure 11b). Obviously, two intermediary kinds of RM exist, which have structures of different densities. This difference levels out later on by intramolecular cross-linking.

Glass Transition Temperature of Reactive Microgels. The T_g of the RM was higher the larger the fraction of styrene was, but also the longer the reaction time was (Table 4). The increase of T_g with reaction time again indicates a continuing intramolecular cross-linking.

Conclusion

Reactive microgels can be prepared by self-emulsifying copolymerization of unsaturated polyester and styrene. If the fraction of the emulsifying polyester is sufficiently large, microemulsions are formed which contain only micelles and no monomer droplets. With an oil-soluble initiator, such as azobis(isobutyronitrile), the initiation of the copolymerization takes place predominantly in the incoherent lipophilic phase. It could be shown[11] that under these reaction conditions the composition of the microgels does not change over the whole time of the reaction and is the same as that of the initial mixture of the reactive components. This constant composition implies that the components of still unreacted micelles do not diffuse to the growing microgel particles.

Not yet initiated micelles are initiated continuously later on and form microgels of essentially the same size as those polymerized before. Such microgels may only increase in size by reacting with other microgels (intermolecular reaction) or by capturing not yet polymerized micelles. Both events have little probability because of the strong electrostatic repulsion between the microgels and respectively microgels and micelles. Therefore, these reaction conditions enable the synthesis of microgels with a uniform composition and a narrow size distribution.

The different reactivities of the unsaturated polyester units and styrene have only consequences for the internal structure of the microgels but not for their composition. Only in the case of an azeotropic mixture of both reactive components may a constant composition of the microgels be expected. As the unsaturated polyester is also the emulsifier of the system, a different mechanism of microgel formation was suspected when the mass fraction of this component is too low.

In order to find out whether these arguments are true, RM from mixtures of smaller fractions of the UP were prepared. Surprisingly, the composition of the microgels remained constant in the case of both mass ratios (70/30 and 60/40), i.e. with smaller fractions of the polyester; however, the appearance of these mixtures changed from that of a microemulsion (bluish and translucent) to that of an obviously coarser emulsion (milky white and opaque). In agreement with this visual indication of an increased size of the incoherent phase of reactive components, the micelle diameter increased by an order of size. Obviously, with a decreasing amount of the polyester, the micelles gradually approach the size of monomer droplets. Contrary to the stable microemulsion from mixtures of the unsaturated polyester and styrene with a larger amount of polyester, smaller polyester fractions also decrease the dispersion stability of the respective microgels. Therefore, aggregates of primary microgels were increasingly formed, the existence of which was indicated by a rise of the particle diameter, the intrinsic viscosity, and the molar mass. With still lower fractions of the emulsifying polyester, styrene molecules eventually may leave their micelles and droplets and diffuse to the growing particles, thus increasing the amount of styrene units in the reactive microgels above that in the initial reaction mixture. However, it is more probable that, in competition with the copolymerization in the micelles, the reactive components are copolymerized in the existing droplets and pastes are formed, because the copolymerization is initiated in the lipophilic phase. The tendency of the droplets, containing cross-linking species, to polymerize is supported by the gel effect.

Preceding considerations raise the question whether in the case of mixtures of unsaturated polyesters and styrene with a decreasing fraction of the polyester a continuous transition of micelles to droplets takes place. This situation is different from that in normal emulsion polymerization, where micelles and monomer droplets coexist.

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