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times to be reliably interpreted in terms of molecular processes.

Experiments are currently being conducted with the labelled polyisoprene chains in order to further our understanding of the influence of solvent power on local segmental dynamics. Preliminary results for a good solvent indicate that there is essentially no molecular weight dependence after overall molecular rotation is taken into account. These results will be reported in the near future.  

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Emulsion copolymerization of hydrophobic with hydrophilic monomers leading to products with anomalous chemical composition distributions

G. H. J. van Doremamele, A. M. van Herk, J. L. Ammerdorffer and A. L. German*

Laboratory of Polymer Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands  
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The particle nucleation mechanism in styrene (Sty)--methyl acrylate (MA) emulsion copolymerization has been studied by means of the experimental determination of the chemical composition distribution (CCD) of the copolymers formed. The various possible loci of particle nucleation (polymer growth) may differ in their monomer concentration regimes leading to different copolymer compositions. Strong indications have been found that the occurrence of a homogeneous particle nucleation mechanism is reflected in the CCD of the Sty--MA emulsion copolymers prepared under conditions of high conversion rates.

(Keywords: t.l.c.; emulsion copolymerization; oligomers; microstructure; particle nucleation)

Introduction

Emulsion polymerization is a very complex process due to the heterogeneity of the system. In 1948 Smith and Ewart proposed a mechanism for emulsion polymerization of hydrophobic monomers, such as styrene (Sty). Subsequently, several more refined mechanisms have been proposed, for instance those taking into account the aqueous phase and (4) monomer droplets. Strong indications were found that emulsion copolymerization involving two monomers of very different water solubility (e.g. styrene--methyl acrylate (Sty--MA)) will exhibit different particle nucleation mechanisms simultaneously, namely the mechanism of micellar entry as well as the homogeneous nucleation mechanism. Guillon showed that monomer partitioning between aqueous phase, latex particles and monomer droplets is the main cause of the large discrepancy between the apparent r-values found in emulsion copolymerizations (based on overall monomer feed ratio data in combination with copolymer compositional data) and the 'real' r-values determined in solution or bulk experiments. The monomer composition drift during emulsion copolymerization could be successfully described using these 'real' r-values in combination with the local monomer ratio inside the latex particles. Thus, the various possible loci of particle nucleation and growth may also be subject to different monomer concentration regimes. Therefore, in the present Sty--MA system, it may be expected that copolymers of different chemical composition will be...
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Figure 1. Observed CCDs of emulsion copolymers of styrene and methyl acrylate. Relative weight ($R_w$) versus the fraction of styrene in the copolymer ($F_{sty}$). The peak area is proportional to conversion. (a) Exp. 1, 21% conversion (-----) and 77% conversion (--); (b) exp. 2, 94% conversion; (c) exp. 3, 20% conversion (-----) and 99% conversion (-----); (d) exp. 4, 90% conversion.

formed simultaneously. These are sufficient reasons to investigate the Chemical Composition Distribution (CCD) of the emulsion copolymers formed. These CCDs may provide important insight into emulsion polymerization nucleation mechanisms.

Experimental

The recipe of the ab initio copolymerizations and the reaction rates in stage II ($R_{pI}$) are shown in Table 1. The copolymer latices were prepared in a 1 litre glass vessel. Before use, the monomers (Merck) were distilled at reduced pressure under nitrogen. Monomers and n-dodecyl mercaptan (Fluka) were added dropwise to a sodium dodecylsulphate (Merck p.a.) solution, thermostated at reaction temperature. Subsequently, a potassium persulphate (Merck p.a.) solution (in 25 ml water) was added to the reaction mixture. The total weight conversion was determined by solid content analyses. The feed ratio was continually monitored by means of gas chromatography. After reaction, the copolymer was isolated and purified from emulsifier, unreacted monomers and initiator by careful coagulation with an aluminium nitrate (Merck) solution (0.001 mol dm$^{-3}$), subsequent decantation and removal of water and coagulant by filtration. The final products were thoroughly washed 10 times with hot water (80°C) and dried at 10$^{-5}$ Torr for at least 8 h. The experimental procedures, including the CCD determination by means of thin layer chromatography/flame ionization detection (T.L.C./F.I.D.), have been described in detail by Tacx$^4$.

Results

Since the water solubility of ethyl methacrylate is far less than that of MA, for the sake of comparison a series of Sty-ethyl methacrylate copolymers was prepared over a wide range of reaction conditions (e.g. temperatures 50–80°C). A typical experiment with a high rate is given as an example in Table 1 (exp. 5). We found that all these Sty-ethyl methacrylate copolymers exhibit monomodal (i.e. 'single-peaked') CCDs. The overall copolymer compositions can be rather well predicted by the well-known Alfrey-Mayo model, using solution $r$-values.

Also the copolymers of styrene (Sty) and methyl acrylate (MA) prepared at moderate reaction rates and starting from a Sty-rich monomer feed composition, showed monomodal CCDs (Figure 1a).

However, at high reaction rates and the same initial feed composition, products with two-peaked CCDs (Figures 1b, c and d) are obtained, indicating anomalous behaviour in Sty-MA copolymerization. Furthermore, as reaction rate increases (by using higher temperature and/or higher initiator concentrations), the distance...
between the two peaks becomes larger. At the same time the fraction of the relatively MA-rich copolymer increases (Figures 1b, c and d). Apparently, the latter copolymer fraction is mainly formed at low conversion (Figure 1c, broken line), whereas higher conversion favours the formation of the relatively Sty-rich product (Figure 1c, solid line). Replacement of the water-soluble potassium persulphate initiator by the oil soluble AIBN (2,2'-azobis-isobutyronitrile) or the amphiphilic ACPA (4,4'-azobis-4-cyanopentanoic acid) did not significantly affect the observed CCDs.

Discussion and Conclusions

In the case of emulsion homopolymerization of hydrophobic monomers, such as Sty, oligomers with only a few monomeric units will already tend to become insoluble in the aqueous phase. These short oligomers will either coprecipitate to form new particles or become incorporated in existing particles, depending upon the emulsifier concentration in the aqueous phase. Therefore, in that case it is very difficult to discriminate between possibly occurring homogeneous and micellar nucleation mechanisms. In the case of hydrophilic monomers the oligomeric length at which precipitation occurs, is considerably larger. For example, according to literature data, oligomers containing up to 65 units of methyl methacrylate are still soluble in the aqueous phase, and this number will probably even be larger for the more hydrophilic monomer MA. These large oligomeric radicals will be stabilized by adsorbing soap molecules resulting in a polyelectrolyte-type complex.

On the grounds of the above-mentioned phenomena the following mechanism is proposed to explain the present anomalous behaviour. In the first instance homogeneous nucleation will occur during stage I of the Sty–MA emulsion copolymerization. The formed oligomeric radicals mainly contain MA due to the high water solubility of MA relative to Sty. Assuming solution kinetics and deriving relevant rate constants from literature data, the maximum average chain length that kinetically can be obtained in the water phase is estimated to lie in between 100 MA and 200 MA units (60°C). However, before reaching this kinetically estimated length, the growing oligomeric radicals will coprecipitate, and then continue to grow in the primary particles under different conditions. The monomer content of these growing primary particles will initially be relatively MA rich. Gradually, a separate phase begins to develop with an increasingly less hydrophilic interior, stabilized by adsorbed surfactant. Coagulation of the soap stabilized primary particles is retarded by electrostatic repulsion. The copolymer formed up to this moment will be relatively rich in MA.

Eventually, latex particles are formed either by coagulation, as the soap concentration decreases, or by growth of the primary particles. The Sty/MA ratio will be higher in the latex particles than in the primary particles. Thus, the fraction of relatively MA-rich copolymer is formed during homogeneous nucleation and primary particle formation, whereas the relatively Sty-rich copolymer is formed during the (further) growth of the latex particles. The discussed mechanism involves the formation of MA-rich copolymer in Smith–Ewart stage I. The present concept explains that at higher reaction rates, when more primary particles are being formed, more MA-rich material is obtained. Also, at higher temperatures the critical oligomeric length will increase and therefore the difference in chemical composition between the two fractions of copolymer molecules will increase. Apparently, the amount of MA-rich copolymer formed at the very beginning of the low rate reactions (i.e. far less primary particles) is too small to be detected in the product at moderate conversion.

Present investigations are aimed at testing this concept by studying different reaction conditions, such as varying monomer ratios, potassium persulphate and sodium dodecyl sulphate concentrations, and temperature. Furthermore, emulsion copolymerizations will be carried out with other monomer pairs differing in water solubility.

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