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Polymer 43 (2002) 7085–7091

polymerwww.elsevier.com/locate/polymer

Anionic dispersion copolymerization of styrene and 1,3-butadiene[☆]

I. Tausendfreund^a, F. Bandermann^{a,*}, H.W. Siesler^b, M. Kleimann^b^aInstitut für Technische Chemie, Universität Essen, 45117 Essen, Germany^bInstitut für Physikalische und Theoretische Chemie, Universität Essen, 45117 Essen, Germany

Received 16 November 2001; received in revised form 9 May 2002; accepted 21 May 2002

Abstract

The anionic dispersion copolymerization of styrene and butadiene was investigated. The suitability of the lower alkanes butane and pentane as dispersing media was tested. Only pentane turned out to be suited for the synthesis of non-aggregated polymer particles. Following block copolymerization experiments, the active chain ends were found to be homogeneously distributed over the whole particle volume by TEM analysis of OsO₄ treated polymer probes. This result contradicts the opinion of Kim et al. [Korea Polym J 7 (1999) 64] who suppose a location of the active centers only at the surface of the polymer particles. Polymer particle aggregation in the synthesis of poly(styrene-*b*-butadiene) and poly(styrene-*b*-butadiene-*b*-styrene) di- and triblock copolymers can be attributed during the early part of butadiene polymerization to the well known association of growing lithium chain ends from separated polymer. Later on, at higher butadiene conversions, an entanglement of longer polymer chains causes agglomeration, too. The most important parameter to obtain a stable poly(styrene-*b*-butadiene)lithium dispersion is the molecular mass of the poly(butadiene) block. The upper limit was evaluated to be 8000 g/mol. For technical applications, this means a maximum of 5 wt% of poly(butadiene) for a total molecular mass of 150,000 g/mol. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Anionic copolymerization; Butadiene; Styrene

1. Introduction

Anionic dispersion polymerization (ADP) in hydrocarbons, which combines the advantages of anionic and suspension polymerization, has been a subject of research during the last few decades [1–3]. It delivers high solid contents in the polymerization reactor at low viscosity of the reaction medium and allows a mechanical separation of the polymers. The further interest arises from the need of uniform size polymer particles combined with the option of particle surface functionality due to the potential for many applications in biomedicine, catalysis, surface coating etc. [4].

Usually block copolymers are used as dispersants in ADP. In one type of process they are synthesized prior to their use. Here, two papers describe the possibility of controlling the particle size and size distribution of poly(styrene) by poly(styrene)/poly(butadiene) di- and triblock copolymers as dispersing agents, and the influence

of reaction parameters like dispersing agent concentration, monomer concentration, initiator concentration, monomer multi-addition and reaction temperature on the time for onset of nucleation [5,6]. Quirk et al. [7] investigated the suitability of the poly(*t*-butylstyrene) moiety as part of poly(*t*-butylstyrene-*b*-styrene) as a dispersant for the formation of a stable dispersion in the anionic homopolymerization of styrene and in the block copolymerization of *t*-butylstyrene and styrene. Another type of process is the so-called living dispersion polymerization (LDP). Here an ADP is performed using a mixture of a simple organolithium compound and a preformed polymeric organolithium compound as initiators for polymerization of vinyl monomers in alkane. Thus, homopoly(styrene) as the core phase and poly(*t*-butylstyryl-*b*-styrene) copolymer as steric stabilizer can be simultaneously produced when styrene is added to a mixture of *sec*-BuLi and poly(*t*-butylstyryl)lithium as initiators [7,8]. Companies like BASF AG and Mobil Oil Corporation protected their results of research in ADP by patents. These patents describe among other topics the production of poly(styrene) as well as block and random copolymers of styrene and butadiene [9–16].

A problem of ADP is the separation of the polymer particles from the dispersing medium. The major part can be

[☆] Part of this article was presented at the Europolymer Congress held in Eindhoven, The Netherlands, 15–20 July 2001.

* Corresponding author.

E-mail address: friedhelm.bandermann@uni-essen.de (F. Bandermann).

separated in a first step by simple filtration, the rest has to be removed by an expensive drying procedure in vacuum. In all papers and patents *n*-hexane was used as dispersing medium. First, we were interested in the question whether *n*-butane and *n*-pentane would be better suited as dispersing medium for ADP due to their higher vapor pressure and lower vaporization enthalpy in comparison with *n*-hexane and due to their lower compatibility with poly(styrene) and poly(styrene-*b*-butadiene) copolymers. Second, Kim et al. [8] postulated for the case of LDP that the polyanions were located only at the outer surface of the polymer particles. We tried to find proofs for such an allocation of the active centers also in the case of ADP by block copolymerization of styrene and butadiene. Third, agglomeration of the polymer particles is sometimes observed in the synthesis of poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymers by ADP. Therefore, we performed some specific triblock copolymerization experiments of styrene and butadiene for a better understanding of this phenomenon.

2. Experimental

2.1. Materials and purification procedures

Styrene was received as a technical product from BASF AG and dried by stirring with LiAlH₄ under reduced pressure for at least 72 h. Afterwards, it was degassed in vacuum for a couple of minutes, saturated with argon (Messer Griesheim, 4.6) and again degassed in vacuum. This procedure was repeated five times. Then the styrene was distilled under reduced pressure. The freshly distilled styrene was kept at low temperature in the darkness and used for the ADP as soon as possible.

The dispersing agent was a diblock copolymer of styrene and butadiene and prepared by anionic polymerization with a total molecular mass of 62,600 g/mol (*D* = 1.05) and 67.55 wt% poly(butadiene) [17]. It was stabilized with 0.5 wt% of Irganox 1076 (Ciba-Geigy).

Butane with a purity of 99.0% was bought from Messer Griesheim, pentane as technical product with a content >95% from Solvents Documentation Synthesis (SDS). Both solvents were purified with a 2.5 M solution of butyl lithium in hexane (Fluka) and directly distilled into a storage tank under an argon atmosphere. These materials were then used as the continuous phase for ADP.

Butadiene (Messer Griesheim 2.0) was condensed into a storage flask, then transferred into an ALOX filled burette. ALOX is a special aluminium oxide for the purification of organic compounds and was received from BASF AG. The butadiene was kept in the ALOX-burette at –30 °C for at least 3 h before use.

In order to terminate the anionic polymerization, methanol (Fluka) which was degassed in vacuum and saturated with argon was used.

2.2. Polymerization

A 1 l glass reactor from Buechi was dried in vacuum at a temperature of 95 °C for at least 5 h. During that time, 6 bar of argon were pressed into the reactor every 20–30 min. Every part of the plant which got in contact with any of the reaction products was dried in vacuum at high temperatures. While butane or pentane and butadiene were directly transferred through 3 mm stainless steel pipes from the purification vessels to the reactor, styrene (which contained the dispersing agent) and *sec*-butyllithium (0.365 M in cyclohexane) were filled in via an argon washed lock-chamber.

To prepare the reaction medium for the homopolymerization of styrene the solution of the dispersant in styrene was charged into the reactor followed by the addition of butane or pentane. The reaction medium was heated up to 45 °C and *sec*-butyllithium (0.365 M in cyclohexane) was pressed into the reactor with a syringe. The solution turned orange within several seconds and after about 1 min nucleation took place. After 2.5 h the polymerization was terminated by addition of 1 ml methanol. The polymer was separated from the continuous phase by vaporization of the solvent (butane) or by sedimentation (pentane) and dried in vacuum.

In the case of synthesis of poly(styrene-*b*-butadiene) diblock copolymers in pentane, butadiene was added in pure form to the reactor after complete conversion of styrene as outlined in the homopolymerization step. The stirred reaction mixture could be observed through a window in the glass reactor. Thus, the point of aggregation of the dispersion could be easily determined. Furthermore the progress of the reaction was followed through the same window by Raman spectroscopy as it is described elsewhere [17,18]. For the synthesis of poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymers as third step, styrene was added after butadiene was used up. However, at first styrene had to be diluted with pentane to prevent a dissolution of the copolymer in the styrene enriched reaction mixture.

During all polymerization experiments samples could be taken from the reactor with a syringe for further analysis.

2.3. Polymer characterization

The composition of the polymers was analyzed by ¹H NMR spectroscopy and the molecular mass was determined by GPC. The ¹H NMR spectrometer was a Gemini 200 (Varian) with a frequency of 200 MHz. One hundred and fifty milligrams polymer were dissolved in CDCl₃ and filled into 5 mm sample tubes. The GPC used a MZ Sdplus column at a CHCl₃ flow rate of 1 ml min⁻¹. A differential refractive detector was used and the calibration was carried out with poly(styrene) standards. The difference in the hydrodynamic volume between poly(styrene) and poly(butadiene) was taken into account with a correction factor of 1.72.

Table 1

Initial values of reaction components in the ADP of styrene with *s*-butyllithium (*s*-BuLi) as initiator in butane and pentane as dispersing media and with a poly(butadiene-*b*-styrene) copolymer as dispersant

| | g | | g |
|-----------------------------|------------------------|-----------------------------|------------------------|
| Butane | 132 | Pentane | 252 |
| Styrene | 45.3 | Styrene | 45.4 |
| Dispersant | 1.1 | Dispersant | 1.24 |
| <i>s</i> -BuLi ^a | 0.483×10^{-3} | <i>s</i> -BuLi ^a | 0.219×10^{-3} |

^a mol/l in cyclohexane.

2.4. Particle characterization

In order to analyze the surface of the particles and the polymer morphology, SEM and TEM were used. The SEM was a Zeiss DSM 960A and used a potential of 15,000 V for the electron acceleration. Electrostatic charge could be avoided by gold plating of the polymer surface.

The TEM microscope was a Zeiss EM 900 with an acceleration potential of 80,000 V. The samples were embedded in epoxy resin, cut to 90 nm slices and contrasted with OsO₄.

3. Results and discussion

3.1. Choice of the dispersant

We decided to use only one special block copolymer of butadiene and styrene as dispersant in all polymerizations. The poly(butadiene) block shows strong interactions with hydrocarbons as dispersing medium, the styrene block with poly(styrene) in the case of a homopolymerization of styrene and with poly(styrene) in the case of a copolymerization of butadiene and styrene. An increase of the polybutadiene content in the block copolymer will lead to an increase in particle swelling and to a decrease of dispersion stability causing an aggregation or a decay of the particles, respectively. For poly(butadiene) a molecular mass between 30,000 and 40,000 g/mol is recommended for an optimal interaction with a solvent [19]. The molecular mass of the poly(styrene) block in the dispersant should exceed 17,300 g/mol for an optimal entanglement with the polymer at the surface of the particles [20]. Thus we synthesized a diblock copolymer of butadiene and styrene by anionic polymerization with a number average molecular mass of 62,000 g/mol for the whole copolymer and of 42,300 and 20,300 g/mol for the poly(butadiene) and poly(styrene) block, respectively.

3.2. Suitability of butane and pentane as dispersing media

From test polymerization experiments of styrene a concentration of the dispersant of 2.5 wt% with respect to

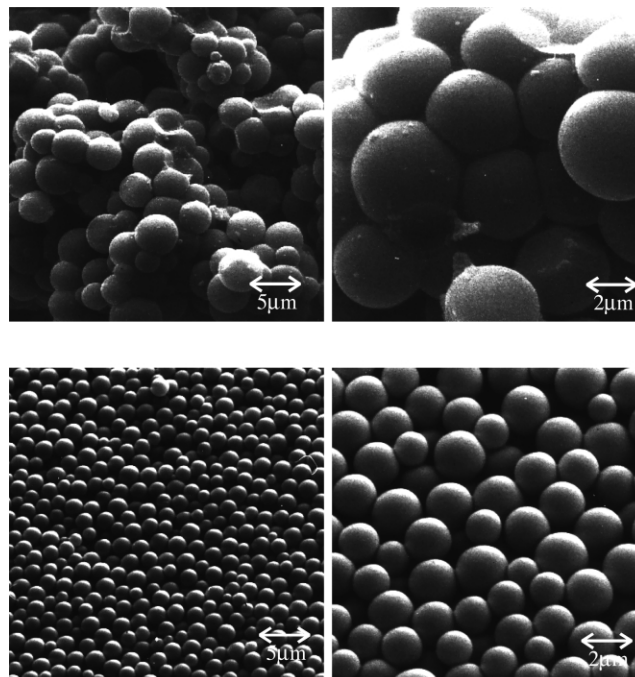


Fig. 1. SEM micrographs of polymer dispersions from the ADP experiments in Table 1. Dispersing media: first row: butane, second row: pentane.

styrene as monomer seemed to be of advantage to obtain a stabilized suspension. However, the dispersant used was hardly soluble in butane and pentane, but when styrene as monomer was polymerized it acted as a solvent at the beginning of the reaction. To get the dispersant dissolved to an opalescent solution a minimal styrene concentration of 21 wt% was necessary for butane and of 7 wt% for pentane. On the other hand styrene acted also as a solvent for the forming poly(styrene). From determinations of phase diagrams for the ternary systems alkane/styrene/poly(styrene) it resulted for 45 °C that the initial styrene concentration must not exceed 31 wt% in the case of butane and 24 wt% in the case of pentane to have the polymer precipitated [17]. The maximal styrene concentration in pentane must be 21 wt% at 65 °C. To enhance the formation of a homogeneous solution at the start of the polymerization the dispersant had at first to be added to styrene where it is easily soluble. The dispersing medium could then be added in the second step. Initial values for all reaction components in two representative experiments are given in Table 1. Fig. 1 shows SEM micrographs of the corresponding polymer dispersions. In both systems spherical polymer particles were formed. However, while they are uniform and very well separated for pentane as dispersing medium, they are partially grown together in butane. For an explanation of these observations it has to be taken into account that the concentration of styrene, which acts also as a cosolvent for the dispersant, decreases during the polymerization. In butane the solvency of the whole reaction medium decreases to such an extent that the butadiene block of the dispersant

Table 2

Amounts of reaction components in the ADP to produce poly(styrene) (A), poly(styrene-*b*-butadiene) (B) and poly(styrene-*b*-butadiene-*b*-styrene) (C) with *s*-butyllithium (*s*-BuLi) as initiator in pentane as dispersing medium with a poly(butadiene-*b*-styrene) copolymer as dispersant

| A | g | B | g | C | g |
|-------------------|------|-------------------|------|-------------------|------|
| Pentane | 252 | Pentane | 252 | Pentane | 252 |
| Styrene | 43.5 | Styrene | 42.6 | Styrene | 47.0 |
| | | Butadiene | 2.9 | Butadiene | 12.1 |
| Dispersant | 1.19 | Dispersant | 1.11 | Dispersant | 1.18 |
| BuLi ^a | 0.44 | BuLi ^a | 0.5 | BuLi ^a | 0.47 |

^a mol/l in cyclohexane.

reaching into the continuous phase becomes more and more insoluble, which leads to an entanglement of the poly(butadiene) chains of at first separated polymer particles and ultimately to an agglomeration. Obviously in pentane the decrease of the solvency of the systems is not so large so that an agglomeration will not occur. So we have to realize that under our conditions butane is not suited as continuous phase in the ADP of styrene though it has been claimed as such in several patents. Therefore we decided to perform all further experiments in pentane as dispersing medium.

3.3. Location of the active centers in the polymer particles

Kim et al. [8] presented results which should prove that in the case of LDP all active centers are only located at the outer surface of the polymer particles. This type of distribution is surprising since it would follow that all polyanions and therefore also all polymer would be enriched in a thin shell at the outer surface of the polymer particles. According to the data the authors presented these particles had a diameter of about 1.5 μm . The number average of the molecular mass of the polymers was between 20,000 and 50,000 g/mol. Thus from the outer surface the polymer chains would reach into the polymer particles only with a length of about 0.036–0.108 μm . Therefore the polymer particles would correspond to balls which are either empty or filled with solvent inside. Both seem to be unlikely.

We tried to determine the active cite distribution over the particle volume in the case of ADP. For that purpose we synthesized poly(styrene-*b*-butadiene) copolymers by a two-step procedure, first polymerizing styrene and then butadiene. The poly(butadiene) block should be built up in the vicinity of the active centers somewhere inside the poly(styrene) formed in the first step. In a styrene/butadiene copolymer OsO_4 reacts selectively with poly(butadiene), blackening the polymer. Due to this selectivity all the black parts in a TEM micrograph of the copolymers would represent poly(butadiene) and correspond to the position of active chains in their reaction with butadiene. Thus the distribution of the active centers over the particle volume could be determined by TEM analysis.

Table 2 summarizes all experimental conditions in the synthesis, Fig. 2 shows TEM micrographs of poly(styrene),

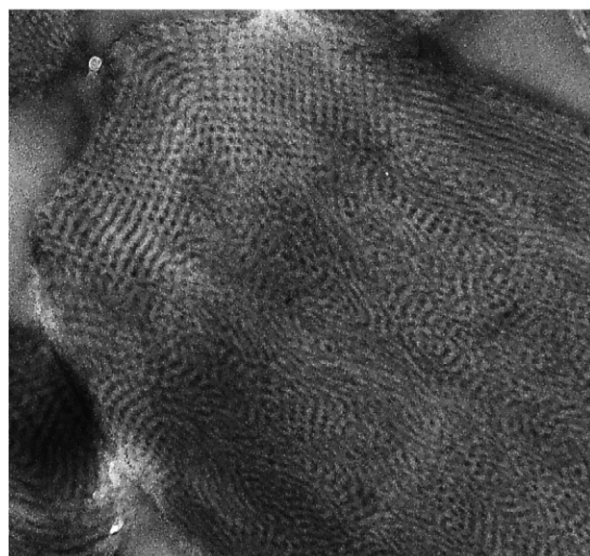
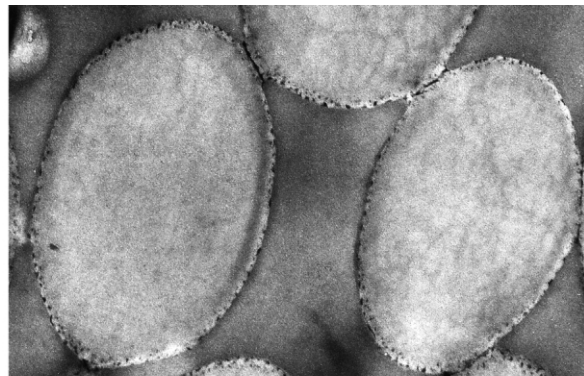


Fig. 2. TEM micrographs of poly(styrene) (top), poly(styrene-*b*-butadiene) (center) and poly(styrene-*b*-butadiene-*b*-styrene) (bottom), synthesized with the value of all variables in Table 2.

poly(styrene-*b*-butadiene) and poly(styrene-*b*-butadiene-*b*-styrene) copolymers.

If all the active chain ends were located on the particle surface, the TEM micrographs would show core shell

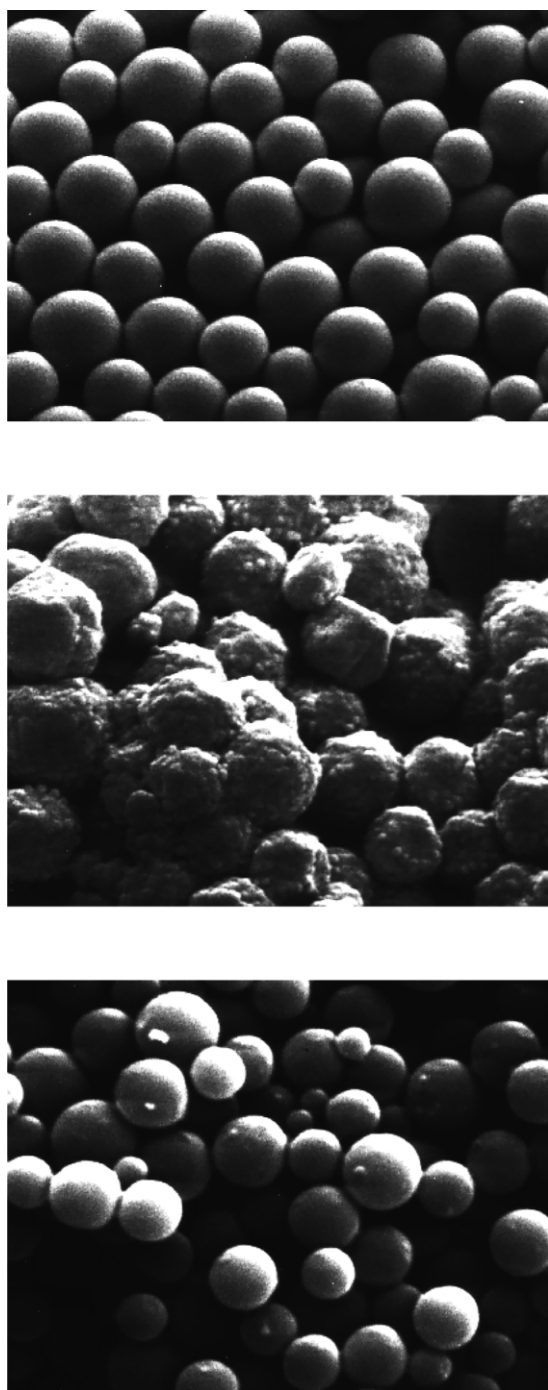


Fig. 3. REM micrographs of poly(styrene) (top), poly(styrene)-*b*-butadiene (center) and poly(styrene-*b*-butadiene-*b*-styrene) (bottom), synthesized by ADP.

polymers in which the first polymerized monomer (styrene) forms the core and the second polymerized monomer (butadiene) the shell. As Fig. 2 shows, no core–shell polymers were produced. Instead of this, black dots (poly(butadiene)) appear in a white matrix (poly(styrene)). Thus, the active chain centers must be well distributed all over the volume of the particle. We assume that the dark ring around the poly(styrene) particles will be due to the

poly(butadiene) block of the dispersant. Thus, the results of Kim et al. cannot be confirmed in the case of ADP. Regarding the analytical methods used by the authors to determine the distribution of the active centers we have serious doubts that the interpretation of the results in the case of LDP is correct.

3.4. Particle aggregation during the synthesis of styrene/butadiene block copolymers by ADP

During the synthesis of poly(styrene-*b*-butadiene) diblock and poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymers by ADP aggregation of the polymer particles in the dispersion is sometimes observed. In contrast to poly(styrene), poly(butadiene) shows strong attractive interactions with alkanes. That is why it is used as one block of amphipathic dispersing agents. The attractive interaction between poly(butadiene) and alkane leads to a swollen state of the particles and finally to an increased solubility of the produced copolymer. Hence, the physical properties, i.e. the stability of the dispersion in ADP, are influenced by the amount of poly(butadiene) incorporated in the copolymer. To attain a better understanding of the aggregation process, samples of poly(styrene), poly(styrene-*b*-butadiene) and poly(styrene-*b*-butadiene-*b*-styrene) were taken from the polymerization reactor and analyzed with REM. The results which are shown in Fig. 3 to document the development of the particle surface during copolymerization. While the surface of the poly(styrene) particle is smooth, the diblock surface is very rough and shows many notches; the poly(styrene-*b*-butadiene-*b*-styrene) surface is smooth again. These observations can be correlated to two aspects. On the one hand, the copolymer is swelling with alkane which softens the surface. On the other hand, after the polymerization of styrene in the first step some growing chain ends are of course located on the particle surface. Poly(butadiene) chains initiated with these active centers will grow preferentially into the continuous phase due to their attractive interaction with the dispersing medium. The active chain ends are very polar lithium organic groups which undergo very strong interactions with other lithium organic groups forming binary and higher associates. At the beginning of the polymerization of butadiene onto poly(styrene)lithium these interactions are only possible between active chain ends of the same particle. With an increase of the length of the poly(butadiene) sequences, the lithium organic groups at the end of the active chains can migrate into the continuous phase and interact with active chain ends of other particles forming associates. This should be the first step of aggregation. The important role of the interaction between lithium organic groups of different particles during beginning aggregation is proven by the fact that termination of these groups with MeOH reduces aggregation completely. In later phases of butadiene polymerization the aggregation can no longer be prevented.

Table 3
Polymer data of samples for agglomeration test

| Styrene (wt%) | Butadiene (wt%) | M_n^a (g/mol) | M_n (PS) (g/mol) | M_n (PB) (g/mol) | Type ^b | T (°C) ^c | Agglom. ^d |
|---------------|-----------------|-----------------|--------------------|--------------------|-------------------|-----------------------|----------------------|
| 90.8 | 9.2 | 26,900 | 24,400 | 2500 | DBC | 45 | No |
| 86.7 | 13.3 | 24,700 | 21,400 | 3300 | DBC | 45 | No |
| 88.6 | 11.4 | 40,700 | 36,000 | 4600 | TBC _s | 45 | No |
| 84.7 | 15.3 | 30,400 | 25,800 | 4700 | TBC _s | 45 | No |
| 80.2 | 19.8 | 25,600 | 20,600 | 5100 | TBC _s | 45 | No |
| 79.7 | 20.3 | 25,100 | 20,000 | 5100 | DBC | 45 | No |
| 93.7 | 6.3 | 90,400 | 84,700 | 5700 | TBC _v | 60 | No |
| 90.1 | 9.9 | 60,800 | 54,800 | 6000 | DBC | 45 | No |
| 85.8 | 14.2 | 43,700 | 37,500 | 6200 | DBC | 45 | No |
| 91.67 | 8.33 | 79,100 | 72,500 | 6600 | TBC _v | 60 | No |
| 69.4 | 30.6 | 27,000 | 18,800 | 8300 | DBC | 60 | Yes |
| 75.1 | 24.9 | 36,500 | 27,400 | 9100 | TBC _v | 60 | Yes |
| 88.1 | 11.9 | 77,700 | 68,500 | 9200 | TBC _v | 45 | No |
| 84.2 | 15.8 | 59,100 | 49,800 | 9300 | TBC _v | 60 | No |
| 81.46 | 18.54 | 68,400 | 55,700 | 12,700 | TBC _v | 60 | Yes |
| 80.97 | 19.03 | 69,900 | 56,600 | 13,300 | TBC _v | 60 | Yes |
| 74.1 | 25.9 | 52,400 | 38,800 | 13,600 | DBC | 45 | Yes |
| 87.9 | 12.1 | 114,000 | 100,200 | 13,800 | DBC | 45 | Yes |
| 92.1 | 7.9 | 183,600 | 169,100 | 14,500 | TBC _v | 60 | Yes |
| 81.9 | 18.1 | 106,100 | 86,900 | 19,200 | TBC _v | 60 | Yes |
| 73.2 | 26.8 | 209,600 | 153,400 | 56,200 | TBC _v | 60 | Yes, strong |

^a Molar mass of total polymer.

^b Process type: DBC, TBC_s, successive synthesis; TBC_v, synthesis process variant.

^c Reaction temperature at formation of poly(butadiene)block.

^d Agglom. = Agglomeration: yes, agglomeration occurred; no, no agglomeration could be observed.

We assume that this is due to an increasing entanglement of longer poly(butadiene) chains growing on the surface of separated particles. In order to get more information about the parameters which are in fact responsible for the aggregation many copolymerizations were carried out. The reaction parameters and the results are listed in Table 3.

Table 3 shows the corresponding values of the molecular mass of the poly(butadiene) block and the observation whether aggregation takes place or not. It is obvious that aggregation could be observed when the molecular mass of poly(butadiene) exceeded 10,000 g/mol even when the poly(butadiene) content in the polymer was as low as 8 wt%. On the other hand, there was no aggregation in any case when the molecular mass was lower than 8000 g/mol even when the poly(butadiene) content was as high as 20 wt%. Neither the absolute percentage of poly(butadiene) nor the reaction temperature both in the range investigated seem to have a higher significant influence on the aggregation. Nevertheless, a high weight percentage of poly(butadiene) should lead to aggregation too, even if the molecular mass is lower than 8000 g/mol, since these polymers should become more and more soluble in pentane due to the attractive interactions between polymer and continuous phase. These contents should at least be higher than 20 wt%.

The bottom micrograph in Fig. 3 shows the surface of poly(styrene-*b*-butadiene-*b*-styrene) which is smooth again. This can be explained with the thesis established before. Swelling polymer and poly(butadiene) chains, which are

migrating off from the surface, lead to a rough surface structure and to aggregation. When the third block of poly(styrene) is formed, the smooth surface is reproduced because of the insolubility of the poly(styrene) blocks both on the surface and in the continuous phase. Consequently, the polymer chains are precipitating and rebuilding a new surface. When aggregation takes place, a smooth surface cannot be expected.

4. Summary

From the lower alkanes butane and pentane, only pentane turned out to be suited as dispersing medium for the anionic dispersion copolymerization of styrene and butadiene. In contrast to the claims in many patents it has to be expected that propane is absolutely unsuitable for such processes.

The active chain ends are homogeneously distributed over the whole particle volume. This result is in contrast to the opinion of Kim et al. [8] who suppose only the surface of the particle to be the place where the lithium organic groups are located. Several contradictions to this statement are discussed in detail elsewhere [18].

Polymer particle aggregation in the synthesis of poly(styrene-*b*-butadiene) and poly(styrene-*b*-butadiene-*b*-styrene) di- and triblock copolymers can be attributed at first to the well known association of growing lithium chain ends from separated polymer particles during the early part of butadiene polymerization. Later on, at higher butadiene

conversions, an entanglement of longer polymer chains causes agglomeration, too. The most important parameter to obtain a stable poly(styrene-*b*-butadiene)lithium dispersion is the molecular mass of the poly(butadiene) block. The upper limit was evaluated to be 8000 g/mol. For technical applications this means a maximum of 5 wt% of poly(butadiene) for a total molecular mass of 150,000 g/mol.

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