Polymer Bulletin 47, 277–282 (2001)

Polymer Bulletin

Synthesis of poly(methyl methacrylate)-g-poly(dimethyl siloxane) graft copolymers via a miniemulsion process

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Received: 12 March 2001/Revised version: 15 September 2001/Accepted: 15 September 2001

Summary

In this article, we describe the synthesis of a PMMA-g-PDMS graft copolymer via a miniemulsion process. A highly hydrophobic PDMS macromonomer was copolymerized in the presence of MMA. Latex particles were obtained with a high yield and a complete incorporation of the macromonomer by using AIBN as initiator, SDS as a surfactant and a PMMA-b-PEO block copolymer as a cosurfactant, with a given amount of methanol in order to reduce the interfacial tension. The characterization of the resulting latex by ^{1}H NMR and QELS evidenced the interest of such a process in order to copolymerize monomers with very different solubilities and to obtain directly a graft copolymer in aqueous dispersion.

Introduction

Graft copolymers are macromolecules of high interest as they can exhibit amphiphilic and compatibilizing properties. Indeed, due to their particular architectures constituted of a main chain and pendant grafts, it is possible to design comb-like graft copolymers of well defined structures. Among the different preparation techniques, the macromonomer technique is one of the most commonly used. Thus, a monomer is copolymerized with an end-capped oligomer terminated with a reactive function (usually an acrylic double bond) that permits the incorporation of the macromonomer into the main polymer chain. Numerous graft copolymers that have been prepared following this method are reported in the literature. However, most of these processes involve solution polymerization that presents the interest of being conducted in homogeneous media [1] [2]. For instance, the synthesis by free radical copolymerization in solution of poly(methyl methacrylate)-g-poly(dimethyl siloxane) (PMMA-g-PDMS) was described by Yamashita et al [3] and Mc Grath et al [4].

Nowadays, for economical and environmental reasons, there is an increasing interest for processes involving emulsion polymerization systems using water as dispersing medium. However, one drawback of emulsion polymerization which is not encountered during homogeneous solution polymerization is the difference of solubility of the monomers, which can lead to dramatic changes in the final composition and properties of the resulting polymer. Indeed, conventional emulsion polymerization described by Smith, Ewart and Harkins implies that the monomer diffuses from the reservoir droplets towards the micelles that are the locus of the polymerization [5] [6]. Thus, in the case of copolymerization, the most hydrophobic monomer has less tendency to be incorporated into the growing macroradicals located inside the micelles. The extreme case is that a completely insoluble monomer can not react at all with a more water soluble comonomer [7]. One possibility to overcome this problem is the miniemulsion polymerization [8] [9]. Miniemulsions are submicronic dispersions of hydrophobic monomers stabilized under high shearing by a conventional surfactant combined with an water-insoluble cosurfactant which is usually a fatty alcohol or a long chain alcane added in order to avoid the well known Ostwald ripening of the emulsion [10] [11]. Consequently, the aim of this work is to demonstrate that the miniemulsion polymerization can be applied to the synthesis of silicon containing graft copolymers by copolymerization of a slightly water soluble monomer such as methylmethacrylate and a very insoluble monomer such as a polydimethylsiloxane macromonomer. Another advantage of this process is that graft copolymers can be obtained directly as an aqueous dispersion.

Experimental part

Reagents :

Azobisisobutyronitrile (AIBN), potassium persulfate ($K_2S_2O_8$) and sodium dodecylsulfate (SDS) were purchased from Fluka and were used without any further purification. Methylmethacrylate (MMA) (Aldrich) was washed with an aqueous solution of sodium hydroxide in order to remove the inhibitor, dried over $MgSO_4$ and distilled under vacuum. Silicon macromonomer (AK5) (molecular weight 5000 g/mol) was purchased from Tagosei Chemical Industry as a solution in a toluene/MEK mixture with a 40% weight concentration. The solvent fraction was removed by evaporation under high vacuum before use. Poly(methyl methacrylate)-b-poly(ethylene oxide) block copolymer PMMA-b-PEO (10-30) with respectively molecular weights of 1000 and 3000 g/mol for each sequence was kindly supplied by Goldschmidt (Germany). Distilled water was used as dispersing medium.

General procedure of the emulsification:

The organic phase (MMA and AK5) was poured in the aqueous phase containing the surfactant system and the miniemulsion was obtained by vigorous stirring (typically 8000 rpm) with an Ultraturax equipment during 15 min under nitrogen atmosphere.

General procedure of the emulsion polymerization :

Polymerizations initiated by adding the initiator and heating the emulsion at 60°C were carried out during 24 hours in order to achieve a complete conversion of the monomers. Typically, the organic phase containing 45 g of MMA and 15 g of AK5 macromonomer was dispersed in 340 ml of distilled water with 4 g of SDS and 2 g of a PMMA-b-PEO block copolymer as cosurfactant. 1 mol% of potassium persulfate or 2 mol% of AIBN with respect to the monomer mixture were used to initiate the polymerization.

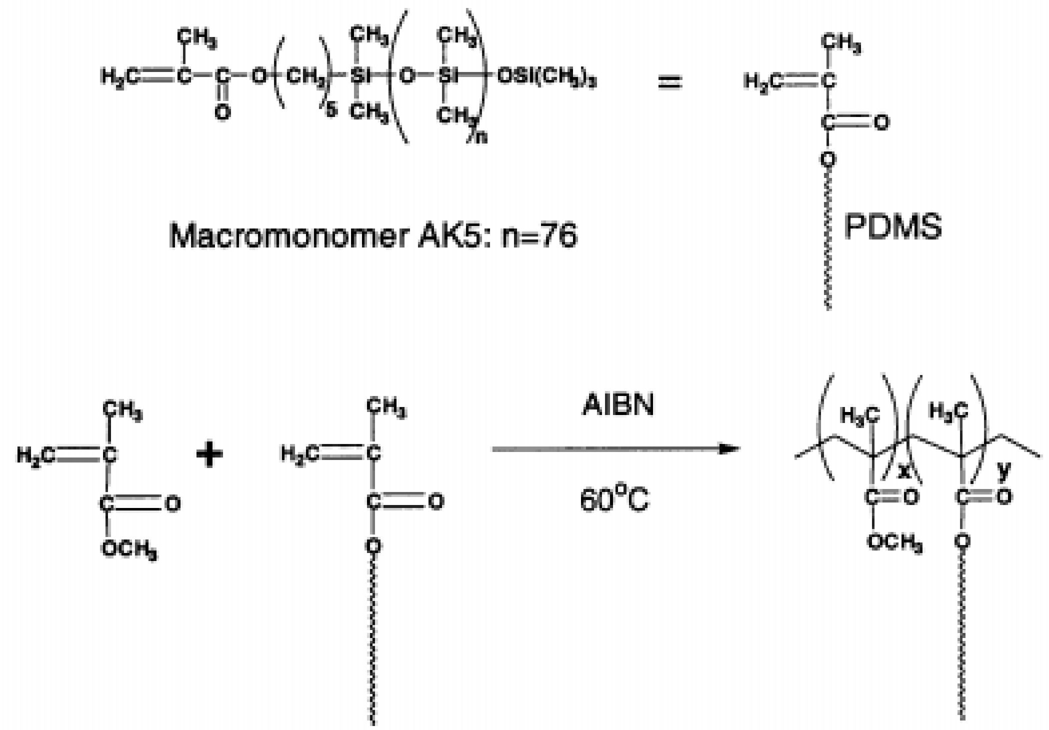
Characterizations

The size distribution of the latex particles was determined by Quasi Elastic Light Scattering (QELS) with a COULTER N4 spectrophotometer. The composition of the PMMA-g-PDMS graft copolymers was performed by ^{1}H NMR with a 250 MHz Brüker spectrometer. Size Exclusion Chromatography (SEC) measurements were performed on a Waters 150 ALC chromatograph calibrated with PMMA standards in THF.

Results and discussion

As mentioned in the introduction, graft copolymers can be synthesized by free radical polymerization using the macromonomer technique. Thus, a commercial polydimethylsiloxane (PDMS) macromonomer (AK5) was copolymerized with methylmethacrylate (MMA) as shown on scheme 1.

Scheme 1: Chemical structure of the PDMS macromonomer and reaction scheme of the copolymerization of AK5 with MMA



For this particular system, classical emulsion polymerization is not a relevant technique for the copolymerization of MMA, that has a relatively high solubility in water (150 mmol/L) and PDMS macromonomer (AK5) which can be considered as totally insoluble in water.

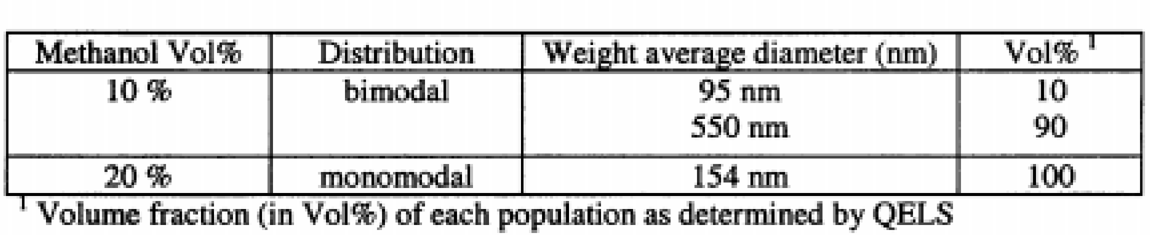
Indeed, a verification experiment showed that the emulsion copolymerization of MMA and AK5 initiated by a hydrophilic initiator such as potassium persulfate leads to a final biphasic product. After complete phase separation, a sample of each phase was taken, dried and analyzed by ^{1}H NMR in order to confirm our assessment: a pure

PMMA latex was formed (lower aqueous phase), the upper phase being constituted of unreacted PDMS macromonomer. This experiment demonstrates that the growth of the polymeric radicals was initiated in the water phase, leaving the totally hydrophobic AK5 unreacted, due to the fact that no transfer of AK5 occurred from the reservoir droplets to the growing latex particles. It is also interesting to point out that a second experiment carried out via a conventional miniemulsion process, that is an emulsion stabilized with SDS and a cosurfactant such as hexadecanol, led to an unstable latex after polymerization initiated by potassium persulfate.

In order to minimize the initiation of the polymerization of MMA in the water phase, an organo-soluble initiator (AIBN) was dissolved into the monomers mixture (MMA and AK5) and dispersed under high stirring with an Ultraturax (8000 rpm) during 15 to 30 min prior to polymerization. The stability of the initial oil in water emulsion was enhanced by using sodium dodecylsulphate (SDS) in combination with a non-ionic polymeric cosurfactant such as a PMMA-b-PEO (10-30) amphiphilic block copolymer. After 24 hrs of reaction, the resulting latex was stable and did not display any phase separation even after several days. However, QELS analysis revealed for the starting emulsion as well as for the final latex a bimodal size distribution with the presence of large particles with a size of about 1300 nm. In a second set of experiments, we decreased the interfacial tension between the organic and the water phase by addition of methanol.

Two identical formulations were prepared with water phases containing respectively 10 vol% and 20 vol% of methanol. The average size and the size distribution of the latex particles in the final polymerized dispersion are reported in Table 1.

Tab. 1. QELS characterization of the final latex



Methanol Vol%	Distribution	Weight average diameter (nm)	Vol% [1]
10 %	bimodal	95 nm 550 nm	10 90
20 %	monomodal	154 nm	100

[1] Volume fraction (in Vol%) of each population as determined by QELS

The initial miniemulsion prepared with 10 vol% of methanol as well as the final latex dispersion (Tab. 1) were still bimodal but with the presence of only submicronic particles. For the smaller ones, e.g. those of 95 nm, it can be assumed that they have derived, at least in part, from the PMMA-b-PEO block copolymer micelles or from micellar aggregates more or less swollen by the monomer. In contrast, the introduction of 20 vol% of methanol showed a significant improvement in the initial emulsion characteristics, since only one population was revealed by QELS in that case. As a consequence the final graft copolymer monomodal latex shows a monomodal size distribution with an average particle diameter of 154 nm and a stability of more than one year. Moreover, latex particles were obtained with high conversion of at least 95%. The resulting dried graft copolymer obtained after evaporating the water phase at 100°C under vacuum was characterized by SEC (M_n=322000 g/mol, polymolecularity index I_p=2) and by ^{1}H NMR (see Fig.1). One can notice the characteristic peaks of the PDMS grafts at 0 ppm and those of the PMMA main chain at 3.6-3.7 ppm with the absence of the typical double bond peaks. The calculated amount of incorporated PDMS macromonomer was found to be 22 wt% as compared

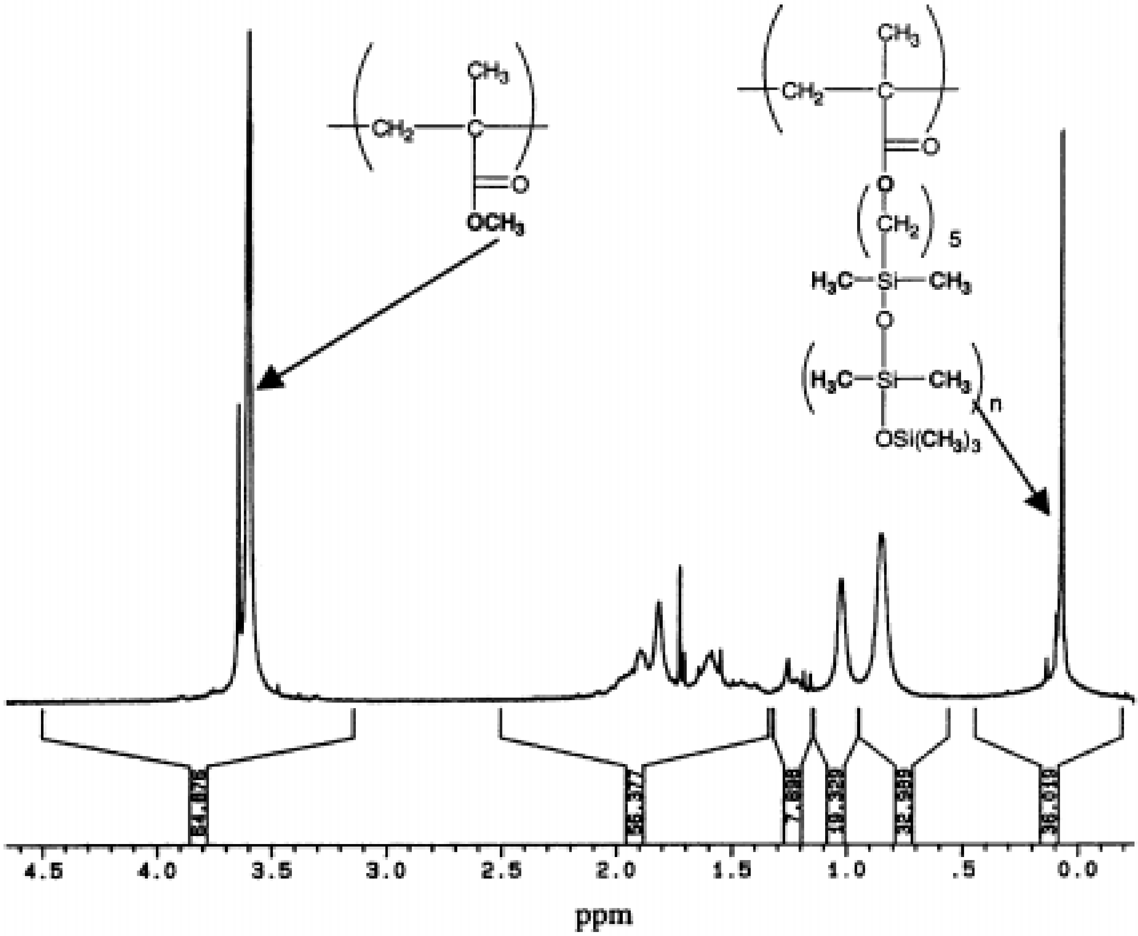


Fig. 1: ^{1}H NMR spectrum of the final dried graft copolymer latex (measurement performed in $CDCl_3$)

to the theoretical value of 25 wt%. Within the experimental error limit, this definitely proves the total incorporation of the PDMS macromonomer in the PMMA main chain.

Conclusion

In this work, we have developed a novel approach to the synthesis of PMMA-g-PDMS graft copolymers containing up to 25 wt% of PDMS by using and improving the so-called miniemulsion polymerization technique that allows, in contrast to conventional emulsion copolymerization to overcome the problem of the difference in water solubility of the two monomers involved in this process. Stable miniemulsions leading to stable and monodisperse graft copolymer latexes have been obtained by using a combination of SDS as a surfactant and of a PMMA-b-PEO block copolymer as a cosurfactant in the presence of a given amount of methanol. The beneficial influences on one hand of an alcohol such as methanol or ethanol and on the other hand of PMMA-b-PEO block copolymers in a miniemulsion polymerization process were recently confirmed by our group [12].

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