Ring-opening Polymerization in Aqueous Emulsion Applied to the Preparation of Interpenetrating Networks Based on Telechelic Polysiloxanes

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SUMMARY : Anionic ring-opening polymerization of 1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclotetrasiloxane (c-PMPS tetramer) was performed by using the new process of aqueous emulsion. Suitable conditions were found which lead to the formation of stable emulsions, and telechelic oligomers with α,ω-SiOH end groups having a remarkably narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n < 1.3$) were obtained. Reproducible results and a tremendous reduction of back-biting reactions are observed by using this very simple process which does not require the drastic purifications of the classical anionic polymerization. Those telechelic PMPS oligomers were used to prepare transparent interpenetrating polymer networks (IPNs) with polybenzyl or polymethylmethacrylate networks.

Introduction

Several interpenetrating polymer networks (IPNs) based on polydimethylsiloxane (PDMS) have been described, which present a nice combination of properties of PDMS and of the other associated network1). In some cases, PDMS has been replaced by polyaromatic siloxanes such as polydiphenylsiloxane2) or polymethylphenylsiloxane (PMPS)3). As a continuation of our work on polysiloxane IPNs4,5), we prepared PMPS / polymethyl or polybenzylmethacrylate IPNs with the aim of improving the mechanical properties of PMPS by reinforcing with polymethacrylates6). This implied the preparation of well-defined telechelic PMPS precursors for the formation of the

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polysiloxane network, which is a difficult challenge as far as the "classical" anionic ring opening polymerization (ROP) of the corresponding cyclosiloxanes is concerned. Anionic ROP of D_4 in aqueous emulsion allowed Hémery et al. to prepare α,ω-diSiOH PDMS with narrow molecular weight distributions ($1.1 < \overline{M}_w/\overline{M}_n < 1.4$), up to high yields[7]. This very simple process was successfully applied to the case of cyclic PMPS trimer and tetramer, and the results are described in this paper.

Results and Discussion

Polymer Synthesis

A 50/50 mixture of the cyclic methylphenylsiloxane trimer and tetramer was obtained by reaction of methylphenyldichlorosilane with ZnO[8]. Pure monomers were recovered by distillation of the mixture. Preliminary experiments of anionic ROMP in aqueous emulsion were performed on the cyclic PMPS trimer and tetramer using the optimal conditions found for D_4[7]. The cyclic monomer was added to a solution of benzyldimethyldodecylammonium hydroxide (NOH) (which acts both as an emulsifying agent and as an initiator) in water in the following proportions : 66 wt % H_2O; 33 wt % cyclic monomer (c-PMPS); 1.3 wt % NOH (4% based on c-PMPS). The mixture was homogenized by sonication for 6 min to break the monomer into droplets forming an emulsion, and the polymerization was carried out at 40°C or higher. However, it was impossible to obtain monodisperse polymers with a good yield, as in the case of D_4, namely because of the lack of stability of the emulsions. Numerous attempts were made in order to form stable emulsions until a more hydrophobic emulsifying agent such as didodecyldimethylammonium hydroxyde (N'OH) was used. The optimal conditions found for the cyclic PMPS tetramer are the following ones : 75 wt % H_2O; 23 wt % c-PMPS; 2 wt % N'OH (8% based on c-PMPS). After sonication of the mixture (6 min), the polymerization was carried out at 95°C. The molecular weights of the polymers recovered after 15 min reaction with 80% yield are listed in Table 1. A good reproducibility of the results is observed.

Table 1. Molecular weights of PMPS obtained by anionic ROP in aqueous emulsion of the cyclic tetramer at 95°C after 15 min reaction.

Run	$\overline{M}_n$ (SEC)[a)]	$\overline{M}_w$ (SEC)[a)]	I_p
1	11 600	20 000	1.7
2	10 000	20 400	2.1
3	14 000	23 000	1.6

a) In CH_2Cl_2, using a polystyrene calibration curve.

The cyclic trimer polymerization was performed under the same conditions but at 40°C, and the results are shown in Table 2. Again, a good reproducibility of the results is observed and the polymer yields are close to 75%. Moreover, the molecular weight distribution is remarkably narrow ($1.2 < I_p < 1.3$) and the molecular weights of those precursors are convenient for the formation of networks in IPNs.

Table 2. Molecular weights of PMPS obtained by anionic ROP in aqueous emulsion of the cyclic trimer at 40°C after 45 min reaction.

Run	$\overline{M}_n$ (SEC)[a)]	$\overline{M}_w$ (SEC)[a)]	I_p	$\overline{M}_n$ (^{29}Si NMR)
4	4 800	5 600	1.2	5 200
5	4 900	6 300	1.3	6 600
6	4 300	5 300	1.2_5	5 800

a) In CH_2Cl_2, using a polystyrene calibration curve.

PMPS Functionality

The titration of the silanol end groups is necessary to confirm the difunctionality of the polymers (absence of macrocycles). The determination of SiOH end groups was performed by quantitative ^{29}Si NMR in the presence of chromium acetylacetonate. The $\overline{M}_n$ values calculated by assuming that each polymer chain contains two SiOH end groups are listed in Table 2. There is a good agreement between $\overline{M}_n$ values determined by two different techniques such as SEC and end group determination.

Silanol end groups of PMPS precursors were reacted with a 5-fold excess of dimethylvinylchlorosilane with imidazole as the HCl scavenger[9)], in order to prepare vinyl terminated oligomers which could be further crosslinked by hydrosilylation with D_4H (tetramethylcyclotetrasiloxane). A quantitative modification was observed as checked by ^{29}Si NMR. Moreover, the vinyl end group determination made by ^{1}H NMR allows another evaluation of $\overline{M}_n$ of these oligomers. The results shown in Table 3 indicate a good agreement between the $\overline{M}_n$ values determined by those different methods. The slight increase of $\overline{M}_n$ observed after modification comes from the fact that the modified polymers were recovered by precipitation in methanol which leads to elimination of some short oligomers.

Table 3. Molecular weights of PMPS oligomers determined before and after chain end modification.

Run	$\overline{M}_n$ (SEC)[a)]	$\overline{M}_n$ (^{29}Si NMR)	I_p	$\overline{M}_n$ (SEC)[a)]	$\overline{M}_n$ (^{1}H NMR)	I_p
	Before modification			After modification		
5	4 900	6 600	1.3	5 800	8 000	1.3
6	4 300	5 800	1.2_5	5 400	7 900	1.3

[a)] In CH_2Cl_2, using a polystyrene calibration curve.

Interpenetrating Polymer Networks

Several strategies were used for the preparation of IPNs based on PMPS and polymethyl or polybenzylmethacrylate. The "in situ" sequential method was adopted in which the formation of the first network takes place at low temperature in the presence of the components of the other polymer network, which is then formed at higher temperature[10,11)]. In a first strategy, the polymethacrylate network was formed by free-radical polymerization of methylmethacrylate (MMA) or benzylmethacrylate (BMA) with a small amount of ethyleneglycoldimethacrylate (EGDMA), with di-t-butylcyclohexylperoxydicarbonate as the initiator at 35°C. The second network was then formed by hydrosilylation of α,ω-divinyl PMPS oligomers with D_4H, in the presence of a Pt catalyst at 65°C. In a second strategy, the PMPS network was formed by condensation of the silanol end groups of the siloxane oligomers with tetramethoxysilane (TMOS), at room temperature, with a catalytic amount of dibutyltindilaurate. The polymethacrylate network was then obtained by free-radical polymerization performed at 70°C with AIBN as the initiator. However, opaque and brittle IPNs were obtained in both cases.

This is why a "mixed" crosslinking agent, such as trimethoxysilylpropylmethacrylate, was used instead of TMOS for the first network formation, which induces some covalent linkages between the two networks. Such a crosslinking agent has been successfully used for the preparation of PDMS/PMMA IPNs12).Transparent IPNs containing around 12 % by weight of extractible material were obtained with 25/75; 50/50 and 75/25 (w/w) PMPS/PMMA compositions as well as for a 50/50 PMPS/PBMA composition. The refractive index of PMPS/PMMA IPNs is comprized between 1.55 and 1.49 (at 21°C). An improvement of the mechanical properties of PMPS is observed in IPNs containing PMMA as shown by the increase of the storage modulus (E') at 25°C : E' being equal to 8.10^7; 3.10^7 and 7.10^8 Pa for 25/75; 50/50 and 75/25 (w/w) PMPS/PMMA IPN compositions respectively.

Conclusion

The anionic polymerization of cyclosiloxanes in aqueous emulsion presents tremendous and spectacular advantages compared to the "classical" anionic ring opening process. This very simple method does not require any special purification of the reagents; experiments are performed in air and a non expensive solvent, i.e. water, is used. Moreover, a reduction of back-biting reactions (leading to a low amount of cyclics) is observed, and telechelic oligomers with narrow molecular weight distributions are obtained with high yields. This allowed us to prepare well-defined networks and IPNs6) as well as block copolymers. The detailed results will be published in a forthcoming paper.

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