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Cyclocopolymerization of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane with styrene

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The copolymerization behaviour of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (DVDS) with styrene in solution, using a free radical initiator, was investigated. Styrene was found to be the more reactive monomer. The *FT*i.r. and ^{29}Si n.m.r. spectra indicated that cyclic units were formed from DVDS in the copolymer, with five- and six-membered ring structures being common. The cyclocopolymerization mechanisms and the thermal properties of the cyclocopolymer are reported. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: cyclocopolymerization; Si-containing polymer; cyclic structure)

Introduction

Organosilicon-containing polymers continue to constitute a fascinating and important class of materials since they exhibit a wide range of properties useful for various technological applications[1–13]. Recently, there has been a considerable amount of interest in the study of polymers containing both silyl and phenyl groups[1,14–19]. In particular, the synthesis and polymerization of styrene derivatives with silyl group(s) have been investigated extensively by Nagasaki *et al.*[1,16–19]. This type of polymer is of great current interest because of their potential usefulness as functional materials such as gas-permeable membranes.

Among all Si-containing polymers, it appears that very few synthesized from α,ω-unsaturated compounds have been studied. Recently, Seyferth and Robison[20] have reported the polymerization of Si-containing monomers of the type $(CH_2{=}CHMe_2Si)_2X$ (where X is O, NH, NCH_3). Their studies have indicated the presence of cyclic units in the polymer chain. One of the reasons for their investigation of cyclopolymers containing a large number of functionalized silicon groups (Si–X–Si groups) is that such polymers are amenable to chemical transformations which may yield a variety of new polymers.

While studies of Si-containing polymers with ring structures, as mentioned above, are focused primarily on the homopolymers, we feel that copolymerization can provide a simple, alternative route for creating novel Si-containing materials with new functionalities and performances. In this communication, we report the cyclocopolymerization of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (DVDS) with styrene (St). The structure, thermal properties and reaction pathways of the cyclocopolymer obtained are also discussed.

Experimental

Synthesis. All chemicals used in this study were reagent grade. The monomers, DVDS (PCR, Inc.) and St (Riedel-deHaen), were distilled under vacuum. The solvent *p*-xylene was received from Riedel-deHaen and distilled under atmospheric pressure. Dicumyl peroxide (Aldrich), which was used as the initiator, was purified by recrystallization. This initiator was chosen as it was more effective than other free radical initiators at the temperature concerned. It should be noted that the reaction temperature of 130°C used in this study was much lower than that of 180°C for the homopolymerization of DVDS reported by Seyferth and Robison[20], using di-*tert*-butyl peroxide as initiator and chlorobenzene as solvent. All monomers and the initiator were stored in a refrigerator before use.

In the preparation of the copolymer, 96 g (24 wt.%) of St, 64 g (16 wt.%) of DVDS, and 236 g (60 wt.%) of *p*-xylene were added to a 500 ml jacketed glass reactor equipped with a stirrer, reflux condenser, sampling hatch, and nitrogen gas inlet. The mixture was freeze–thaw-degassed twice, blanketed with nitrogen, and then heated by the circulation of mineral oil thermostatted at 130.0 ± 0.1°C. When the polymerization system reached 130°C, 4.8 g of the initiator (3 wt.% of the monomers) were charged. At different intervals during the copolymerization process, samples of about 1 g of reaction mixture were withdrawn, cooled quickly, and the reaction was then terminated with 5 drops of 1% hydroquinone/methanol-*p*-xylene solution. The samples were treated with another 1 ml of methanol to precipitate the polymer, heated to evaporate the solvent and the residual monomers, and finally dried to constant weight at 95 ± 2°C for over 72 h under vacuum.

Characterization. The total conversion for each sample was determined gravimetrically. From the ^{1}H n.m.r. spectra, using a Bruker DPX-400 spectrometer operated at a field of 400 MHz in the Fourier transform mode, cumulative copolymer compositions were obtained. Measurements were externally referenced to TMS, with chloroform used as an internal standard. Signals were observed at $\delta(\text{ppm}) = -0.9 - 0.3$ ($SiCH_3$), 0.3–2.7 (aliphatic), 5.3–6.2 (olefinic) and 6.2–7.6 (phenyl group). In the calculation of the cumulative copolymer composition, the phenyl group content from the initiator and hydroquinone were deducted. From the total conversions and the cumulative copolymer

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compositions, the conversions for each monomer were determined. The ^{29}Si n.m.r. spectra with inverse gated decoupling were obtained, using the Bruker DPX-400 spectrometer operated at 79.49 MHz, in $CDCl_3$ with the addition of a relaxation agent $Cr(AcAc)_3$ and externally referenced to TMS. Signals were observed at δ(ppm) = −4.0 ($SiCH{=}CH_2$, br), 8.7 (Si–O–Si in acyclic units, vb), 13.9 (Si–O–Si in six- and/or seven-membered rings, vb), and 24.9 (Si–O–Si in five-membered rings, vb).

The *FT*i.r. spectra (Nicolet Magna IR™-750; from 400 to 4000 cm^{-1}) were obtained from samples prepared as films on potassium bromide (cm^{-1}): 3026 (s); 2924 (s, br); 2851 (m); 1600 (benzene ring, s); 1493 (s); 1453(s); 1406 (w); 1253 (s, $Si{-}CH_3$); 1055 (s, br, Si–O–Si acyclic structure and/or seven-membered ring); 1030 (s); 1002 (m); 992 (m, Si–O–Si six-membered ring); 920 (m, Si–O–Si five-membered ring); 908 (m); 837 (s); 786 (s); 758 (s); 699 (s); and 540 (m).

Molecular weight determinations were made at 25°C by gel permeation chromatography (g.p.c.) using a Waters™ system comprising a U6K injector, a model 510 HPLC pump, a model 410 differential refractometer and a model 820 Maxima Dynamic Solutions Division control system. The gel permeation chromatograph was equipped with a series of two columns: a Polymer Laboratories 5 μ PL-GEL Mixed-C column and a 10^3 Å column; the flow rate of the HPLC grade THF eluting solvent was 1.0 ml min^{-1}. Retention time calibration was carried out using monodisperse polystyrene standards.

A Perkin-Elmer DSC 7 instrument was used to determine the glass transition temperatures of the samples. The helium gas flow rate was 20 cm^3 min^{-1}, and the heating rate was 10°C min^{-1} in all cases. Before starting the heating cycle, the samples were heated to 200°C, held at this temperature for 2 min, then cooled at about 100°C min^{-1} to the start temperature. The temperature interval scanned was from −100 to 150°C for the homopolymers and 10–200°C for all the copolymer samples.

Results and discussion

The glass transition temperatures as determined by d.s.c. for the homopolymers of DVDS and St, which were synthesized using similar recipes at 130.0 ± 0.1°C for 540 min, were −10.0°C and 88.7°C, respectively. When polystyrene ($\bar{M}_w = 2.43 \times 10^4$ and $\bar{M}_w/\bar{M}_n = 2.68$) was blended with poly(DVDS) ($\bar{M}_w = 2.64 \times 10^3$ and $\bar{M}_w/\bar{M}_n = 1.86$) in 3:1, 1:1 and 1:3 weight ratios, the mixtures were found to show two T_g values identical to those of the homopolymers. The data indicate that the homopolymers are immiscible. The sample of polymerization of St and DVDS prepared after 540 min of reaction ($\bar{M}_w = 1.16 \times 10^4$ and $\bar{M}_w/\bar{M}_n = 2.33$) nonetheless showed only a single T_g value between those of the homopolymers. When this sample was blended with the homopolymers in a 1:1:1 weight ratio, however, three T_g values were obtained. The data thus verified that copolymer was indeed formed in the polymerization of St and DVDS.

Figure 1 shows the variations of the total conversion and conversion of each monomer with time. During the copolymerization process, there existed a relatively short initial stage of only a few minutes. At about 50% total conversion, however, the polymerization rate started to slow down. From *Figure 1*, it can also be seen that the conversion of St was greater than that of DVDS, indicating that St is more reactive than DVDS. Above 50% total conversion, there was actually a lot of residual DVDS in the polymerization system as more than 92% of the St monomer had already reacted. Due to the lower reactivity of DVDS, it was difficult for the residual monomers to continue the copolymerization, and therefore the total conversion remained relatively constant for a long time. After 720 min of reaction, we raised the temperature of the polymerization system to 139°C for 4 h, then added another 1.6 g (1 wt.% of the monomers) of initiator and held the temperature for another 6 h. Nonetheless, the conversion of DVDS and the total conversion increased only slightly. In general, the content of DVDS in the copolymer was comparatively low due to the lower reactivity of DVDS, and the T_g values of the copolymer samples were therefore closer to the T_g value of polystyrene than to that of poly(DVDS). With longer reaction times for the copolymerization, more residual DVDS was available for reaction with St, and thus the DVDS content in the copolymer increased with longer reaction time, higher temperature and additional initiator. In the final copolymer sample, the DVDS content was found to be 20.6 wt.%.

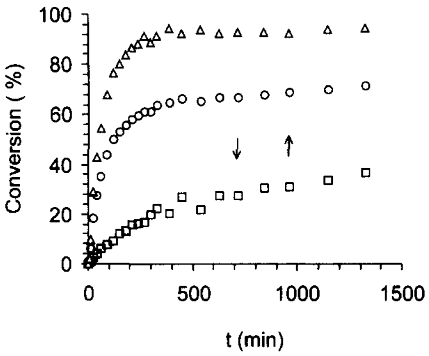

Figure 1 Plots of per cent conversion *versus* reaction time: (○) total conversion; (□) conversion of DVDS; (△) conversion of St; (↓) temperature increased to 139°C; and (↑) additional initiator added

Studies of the solution homopolymerization of DVDS have been reported recently by Seyferth and Robison[20]. Their investigations have indicated the presence of five- and six-membered rings, and possibly also of seven-membered cyclic and acyclic units in the polymer chain. In the present study, cyclization also occurred in the copolymerization, and the existence of cyclic units in the copolymer can be observed in the *FT*i.r. and ^{29}Si n.m.r. spectra. From previous analyses of the i.r. spectra of 2,2,5,5-tetramethyl-1-oxa-2,5-disilacyclopentane[21], 2,2,6,6-tetramethyl-1-oxa-2,6-disilacyclohexane[22], 2,2,7,7-tetramethyl-1-oxa-2,7-disilacycloheptane[21,22] and poly(DVDS)[20], the *FT*i.r. bands at 920 cm^{-1}, 992 cm^{-1}, 1055 cm^{-1}, 1253 cm^{-1}, and 1600 cm^{-1} can be assigned to the presence of Si–O–Si five-membered rings, six-membered rings, acyclic units and/or seven-membered rings, $Si{-}CH_3$, and phenyl groups, respectively. As with the ^{29}Si n.m.r. spectra of $Me_3SiOSi\ Me_3$[23] and Poly(DVDS)[20], δ(ppm) = −4.0, 8.7, 13.9 and 24.9 can be attributed to the presence of $SiCH{=}CH_2$ groups, Si–O–Si in acyclic units, six- and/or seven-membered rings, and five-membered rings, respectively.

In the present system, however, direct quantitative analysis of the different structural components in the copolymer is difficult due to the overlap of some regions in the spectra. Nonetheless, when the ratio of the *FT*i.r. band intensities ($R_{FTi.r.}$) of the five-membered ring (920 cm^{-1}) and the phenyl group (1600 cm^{-1}) was plotted against the molar ratio ($R_{n.m.r.}$) of the Si–O–Si five-membered rings and

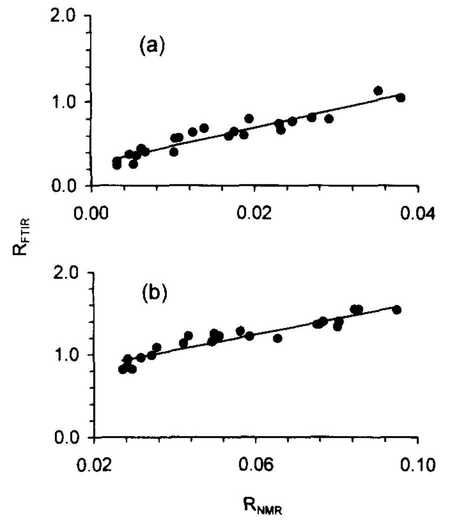

Figure 2 Relationship between the ratio of the *FTi.r.* band intensities ($R_{FTi.r.}$) and the molar ratio of the structural components ($R_{n.m.r.}$). (a) $R_{FTi.r.}$ for bands at 992 cm^{-1} and 1600 cm^{-1} versus $R_{n.m.r.}$ of the six- and/or seven-membered rings and the phenyl group; (b) $R_{FTi.r.}$ for bands at 1055 cm^{-1} and 1600 cm^{-1} versus $R_{n.m.r.}$ of the acyclic units and the phenyl group

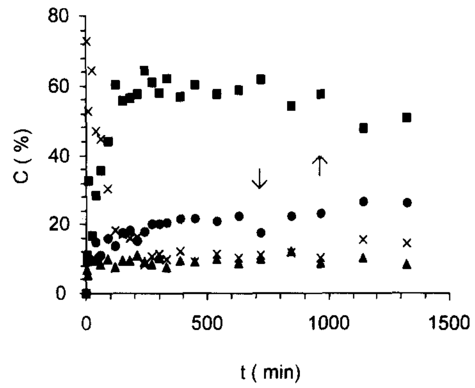

Figure 3 Comparison of the relative amounts of DVDS (C) forming different structural components at different reaction times: (■) unsaturated acyclic units; (•) six-membered rings; (×) saturated acyclic units; (▲) five-membered rings; (↓) temperature increased to 139°C; and (↑) additional initiator added

the phenyl groups in the copolymer, an almost linear relationship (correlation coefficient, 0.948) was found. The $R_{n.m.r.}$ above was determined from the molar ratio of all Si–O–Si structural components formed from DVDS to the phenyl group (obtained from the ^{1}H n.m.r. spectra) times the molar fraction of the Si–O–Si five-membered cyclic units in all the Si–O–Si structural components (obtained from the ^{29}Si spectra).

Although the above correlation between the i.r. and the n.m.r. spectroscopic data is not surprising, a similar result was observed for the plot of $R_{FTi.r.}$ for bands at 992 cm^{-1} (six-membered ring) and 1600 cm^{-1} *versus* $R_{n.m.r.}$ of the 'six- and/or seven-membered rings' ($\delta_{Si} = 13.9$ ppm) and the phenyl group. One possible explanation for this result is that the content of the seven-membered cyclic units is either very low or zero in the copolymer, i.e. $\delta_{Si} = 13.9$ ppm is due mainly to the six-membered rings. If such an explanation is correct, one would expect that a linear relationship also exists in the plot of $R_{FTi.r.}$ for bands at 1055 cm^{-1} (acyclic units and/or seven-membered rings) and 1600 cm^{-1} *versus* $R_{n.m.r.}$ of the acyclic units ($\delta_{Si} = 8.7$ ppm) and the phenyl group. *Figure 2* shows the plots for the latter two cases; the correlation coefficients for the linear regression lines in *Figure 2*(*a*) and 2(*b*) are 0.946 and 0.943, respectively. From this figure, it is reasonable to deduce that there are few or no Si–O–Si seven-membered rings in the copolymer. This result obtained by indirect comparisons of the spectroscopic data also suggests that the cyclocopolymerization reaction pathways mainly follow those of radical initiation with the diene which yield five- and six-membered cyclic units from the thermodynamically more stable secondary radical[20].

The relative amounts of DVDS forming different ring structures and acyclic units in the copolymer samples, as determined from the ^{29}Si n.m.r. spectra, are shown in *Figure 3*. In this figure, it can be seen that a relatively large amount of DVDS reacted to form acyclic units (both saturated and unsaturated) in the early stage (0–100 min) of the reaction. It appeared that the higher polymerization rate at this stage favoured DVDS to form acyclic units, especially the saturated ones. As the reaction proceeded, the portions of DVDS forming different structures remained quite stable, with the percentage in the order unsaturated acyclic units (around 58%) > six-membered rings (around 21%) > saturated acyclic units (around 11%) > five-membered rings (around 10%), although it appears that the percentage of DVDS forming six-membered rings increased slightly and that forming unsaturated acyclic units decreased after 720 min of reaction when the temperature was raised and more initiator was added. Further studies in connection with this work are in progress.

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