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Preparation and Structure of Crosslinked Poly(Methyl Methacrylate-co-1,3-Bis-(Methacryloxymethyl)-1,1,3,3-Tetramethyl Disiloxane)

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Summary

An investigation is presented of the swelling, thermal and morphological characteristics of copolymers of methyl methacrylate and 1,3-bis-(methacryloxymethyl)-1,1,3,3-tetramethyl disiloxane. These materials were prepared by copolymerization/crosslinking of the two monomers by gamma irradiation. Studies were performed on copolymers with mole fraction of the silicon-containing monomer ranging from 0.09 to 0.42.

Introduction

Copolymers of methyl methacrylate and siloxane derivatives present interesting permeation properties and have been proposed as potential polymers for contact lens applications (LIPPMAN, 1981, PEPPAS, 1982). More specifically it has been suggested that high permeability of oxygen can be achieved, although these are glassy materials, due to the considerable contribution of the -Si-O-bonds to the solubility of oxygen in the films (LIPPMAN, 1981). Attempts by various investigators to prepare these materials (MERKER and NOLL, 1956, MERKER and SCOTT, 1957, ANDRIANOV et al., 1957, GREGOREVA and REIKHSFEL'D, 1964) have not given much information about the structure and morphological characteristics of these systems. Here we present a detailed analysis of a copolymer of methyl methacrylate and a disiloxane derivative.

Monomer Preparation

The silicon-containing monomer, 1,3-bis(methacryloxymethyl)-1,1,3,3-tetramethyldisiloxane (BMTDS), was synthesized in a two-step reaction following a modification of the technique of ANDRIANOV et al. (1957).

Into 400 ml of distilled water, 50 gr of chloromethyl dimethylchlorosilane (Pierce Chemical Co., Rockford, Illinois) were added. The mixture was stirred for 8 hours and the organic layer was separated from the aqueous layer. The organic layer was dried using anhydrous Na_2SO_4 and it was found to be pure 1,3-bis (chloromethyl)-1,1,3,3-tetramethyldisiloxane (BCTDS) at

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a yield of 89%. The NMR spectrum of the product was 0.22 δ (s, 12H, $-CH_3$), 2.78 δ (s, 4H, $-CH_2-$).

In a second vessel, sodium methacrylate (37.1 gr, 0.34 mole) was added to an agitated mixture of methacrylic acid (67g, 0.78 mole) and hydroquinone (4 gr) at the reflux temperature; the rate of addition of sodium methacrylate was slow so that rapid solution of the salt could be obtained. BCTDS (36 gr, 0.16 mole) was then added over a period of one hour and the mixture was refluxed for three more hours. The sodium chloride was removed by filtration and the filtrate was diluted with equal volume of benzene. About 200 ml of distilled water were added to the benzene solution. Sodium bicarbonate powder (66 gr, 0.78 mole) was added gradually to the above mixture which was well stirred. After the evolution of carbon dioxide had ceased, the whole mixture was transferred to a separatory funnel and the aqueous layer was removed. The benzene layer was dried over anhydrous Na_2SO_4 and this solution was fractionally distilled under reduced pressure after adding 4 gr of hydroquinone. The fraction with boiling point range 195-196°C/4.3 mmHg was collected. This fraction contained usually co-distilled hydroquinone which was removed by extraction with a 10% aqueous solution of NaOH until the aqueous layer was colorless. The organic layer was dried over anhydrous Na_2SO_4 and identified as the desirable monomer BMTDS. The yield was 50°C. The NMR spectrum of this product was: 0.17 δ(s,14H, $-CH_3$), 1.7 δ(d, 6H, $C = C - CH_3$), 3.86 δ(s, 4H, $-CH_2$), 5.6 δ(m, 2H, $-C{=}C-H$) and 6.17 δ(m, 2H, $-C{=}C-H$). Its density at 25°C was 0.994 gr/cm^3 and the refractive index at 25°C was 1.443.

Preparation of Copolymers

Mixtures of BMTDS and vacuum-distilled methylmethacrylate (MMA) were prepared at mole fractions of BMTDS of $f_1 = 0.1$, 0.2, 0.3, 0.4 and 0.5. They were placed in plastic vials with screw-caps, sealed under nitrogen atmosphere and irradiated in a Co-60 source delivering 5735 rads/min. Total γ-irradiation dose varying from 0.57 to 1.14 Mrads was used for the initiation of the copolymerization and crosslinking reaction and the reaction temperature was kept constant at 60°C or 85°C.

Polymer Characterization

The bulk copolymerized products were received as transparent cylinders which were cut in thin films of thickness 1 mm or smaller using a lathe. Elemental analysis by the modified ashing technique was used to determine the Si content of these copolymers.

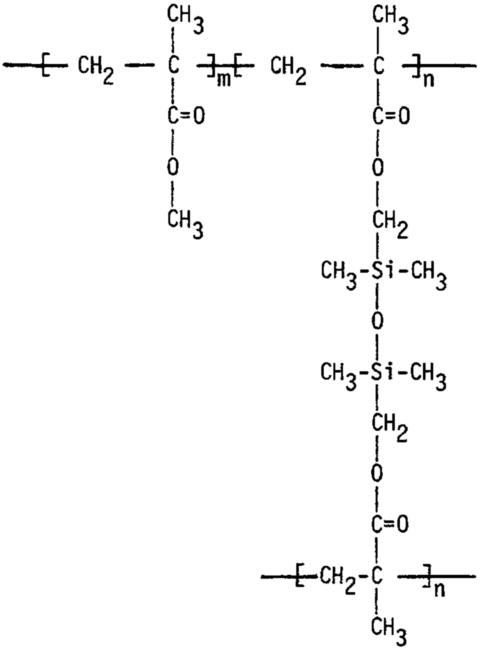
Electron microscopic investigations were performed using a JEX 100 CX transmission electron microscope (Japan Electron Optics Lab, Tokyo, Japan). Copolymer samples of comonomer feed fractions $f_1 = 0.2$ and 0.5 were stained with 1% aqueous solution of OsO_4 for 2,6 and 16 hours. The samples were embedded in an epoxy resin (Epon 812) and cut with an ultra-microtome at 600 Å. Observations were made with 100 keV electrons at magnifications ranging from 10,000 to 290,000 X.

Thermomechanical analysis was performed using a TMS 2 equipment (Perkin Elmer, Norwalk, Conn.). The sample chamber was purged with He and thermal analysis was performed from -150°C to + 150°C at a scanning speed of 1.25 °C/min and at loading of 1.0 gr.

Finally, swelling studies were performed in methylene chloride, chlorobenzene and ethyl acetate, which are known solvents for both homopolymers.

Copolymer Structure

The copolymer produced by this reaction, poly(methyl methacrylate-co-1,3-bis-(methacryloxymethyl)-1,1,3,3-tetramethyl disiloxane), is a crosslinked, amorphous network of varying degree of crosslinking depending on the content of added BMTDS. Its structure is shown below.



(A)

The silicon-containing chain (A) serves as a crosslinking bridge between two longer PMMA polymer chains in loosely crosslinked systems, and becomes part of the overall crosslinked structure in highly crosslinked ones. The copolymer is transparent, hard and insoluble in most organic solvents.

The mole fraction of BMTDS in the copolymer, F_1, was determined by elemental analysis of all prepared copolymers and is presented in Table 1. The same Table presents the swelling characteristics of these copolymers in the three swelling agents studied. Samples with $F_1 = 0.09$ developed crazes during swelling, especially in methylene chloride, where this occurred in a few hours, leading to fragments of swollen copolymer. Less crazing was observed with copolymers of $F_1 = 0.30$ and 0.42. In the last two cases the equilibrium weight, swelling ratio at 25°C, q, was determined as 1.34 and 1.21 gr gel/gr of dry copolymer respectively. In all cases the copolymers swelled, but crazing was not observed for some grades swollen in chlorobenzene and ethyl acetate. These swelling characteristics are indicative of highly crosslinked structures and the crazing may be interpreted as anomalous (non-Fickian) transport of the swelling agent in the amorphous polymers. Crazing is predominant with copolymers of high MMA content.

TABLE 1

Analysis and Swelling Behavior of Copolymers of BMTDS and MMA

Feed Mole Fraction of BMTDS f_1	Copolymer Mole Fractions F_1	T_g (°C)	Swelling Behavior in		
			Methylene Chloride	Chloro-benzene	Ethyl Acetate
0.10	0.09 ± 0.005	120	++	+	+
0.20	0.17 ± 0.01	121	++	+	+
0.30	0.24 ± 0.02	123	+	+	+
0.40	0.30 ± 0.02	---	q=1.34	-	-
0.50	0.42 ± 0.01	122	q=1.21	-	-

++ crazing, + minor crazing, - no crazing

Electron microscopic studies were undertaken to determine whether phase segregation could have occurred in these systems. The results of the analysis of copolymers with F_1 = 0.09 and 0.17, stained with OsO_4 did not show any phases or microdomains.

Glass transition temperatures, T_g, were obtained for all copolymers using thermomechanical analysis. Despite the increase of BMTDS content, the glass transition temperature increased from 120°C to 123°C suggesting a crosslinking effect on the mobility of the chains. Indeed the values of T_g where above that observed for pure poly(methyl methacrylate) (T_g= 112 ± 1°C) obtained by the same radiation-induced polymerization in the absence of silicon-containing monomer. Samples analyzed at subambient temperatures and up to -150°C did not show a low temperature T_g. These results do not preclude the existence of a phase segregated system. However, if that exists it must be of extremely small domain size. Further analysis is in progress to verify this point.

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