CYCLIC POLYMERIZATION OF ORGANOSILICON DIMETHACRYLATE ESTERS

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It is known [1] that many organic monomers that contain unconjugated C=C bonds are capable of forming polymers of cyclolinear structure on polymerization in solution. In particular, polymers with this sort of structure were obtained in the polymerization of dialkyldiallylsilanes.

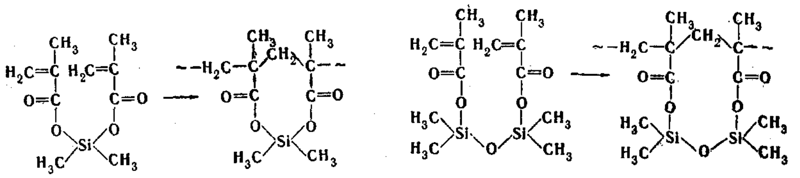
For the first time we have established that the previously synthesized [2] organosilicon dimethacrylate esters of the general formula

$$CH_2{=}C(CH_3)COOSi(CH_3)_2{-}[OSi(CH_3)_2{-}]_n{-}OCO(CH_3)C{=}CH_2$$
$$n = 0.3$$

form polymers (40-80% yields) that are soluble in dimethylformamide (DMF) and swell in tetrahydrofuran (THF), dioxane, and cumene when 5% benzene solutions of them are polymerized at 60-75° C in the presence of 0.5-2.0% benzoyl peroxide. According to the results of analysis and the IR spectra, they contain practically no free double bonds, and their elementary composition corresponds to the C, H, and Si content in the starting monomers.

The polymer of dimethylsilyl dimethacrylate (DMSDMA) (n = 0) has a softening point (according to the Institute of High-Molecular-Weight Compounds [3]) of 162° and an $[\eta]$ value of 0.35 g/100 ml in DMF. The polymers of α,β-dimethacryloxytetramethyldisiloxane (DMATMDS) (n = 1) have a softening point of 195° and, depending on the polymerization conditions, $[\eta]$ values of 0.59 and 0.68 g/100 ml. All of the polymers are very readily hydrolyzed by water to give polymethacrylic acids and the corresponding substituted silanediols. Judging from the intrinsic viscosities ($[\eta]$), the molecular weights of the polymers may amount to $1\text{-}1.5 \cdot 10^5$.

The properties of the polymers enumerated above and the character of their thermomechanical curves, which is not typical for cross-linked polymers, make it possible to assign a cyclolinear structure to them. The structure of the heterocycles has not yet been accurately established. When polymerization occurs via a cyclic mechanism, the addition in the intramolecular step of the polymerization could proceed not only via the "head-to-tail" principle but also by different means. In this connection, one might expect the formation of polymers containing heterocycles with seven, eight, or nine atoms in the polymer chain in the polymerization of DMSDMA, while polymers containing 9, 10, or 11 atoms in the polymer chain might be expected in the case of DMATMDS. The structures of the cyclic links of the polymeric chains of poly-DMSDMA (I) and poly-DMATMDS (II) are presented in the scheme below for the polymerization of these monomers via a "head-to-tail" scheme.



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