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potential scan rates of 5, 10, and 20 mV/s. These voltammograms confirm that the electroactivity of the quinone moieties is maintained after covalent attachment to the siloxane polymer backbone. The results for polymer IV consist of widely separated anodic and cathodic peaks, indicating a high degree of electrochemical irreversibility. For a scan rate of 10 mV/s, the anodic peak potential (E_{pa}) is +0.555 V (vs SCE) and the cathodic peak potential (E_{pc}) is −0.215 V, giving a peak separation (ΔE) of 770 mV; these values are dependent on the scan rate, as shown in Figure 1. The redox behavior of the benzoquinone/hydroquinone system is quite sensitive to the electrode and solution conditions,[19–22] so for comparison we also performed cyclic voltammetry experiments for unbound methylhydroquinone in the 1:1 acetonitrile–water solution. The results are very similar to those found for the polymeric system, with E_{pa} = +0.548 V and E_{pc} = −0.065 V, indicating only slightly more reversible behavior for the unbound species. The voltammetric results for polymer VIII shown in Figure 1 (E_{pa} = +0.350 V and E_{pc} = −0.250 V for a scan rate of 10 mV/s) are also very similar to those measured for the unbound 1,4-naphthohydroquinone species (E_{pa} = +0.330 V; E_{pc} = −0.205 V) under the same conditions.

These results demonstrate that these newly synthesized siloxane copolymers containing hydroquinone and 1,4-naphthohydroquinone maintain the electroactivity of the unbound quinone moieties. In order to test the utility of these siloxane polymers for enzyme-based amperometric sensors, an electrode was constructed by thoroughly mixing 100 mg of graphite powder with 1.0 mg of the polymers, 10.0 mg of glucose oxidase, and 20 μL of paraffin oil, and the resulting mixture was blended into a paste. The paste was packed into a glass tubing (6-mm inner diameter). The preliminary result indicated that these polymers efficiently mediate the charge transfer from reduced flavoenzyme to a conventional electrode surface.

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Registry No. II, 19754-22-4; V, 10075-62-4; VI, 123597-09-1; $BrCH_2CH{=}CH_2$, 106-95-6; $(CH_3O)_2SO_2$, 77-78-1; 1,4-dimethoxybenzene, 150-78-7; 1,4-dihydroxynaphthalene, 571-60-8; glucose oxidase, 9001-37-0.

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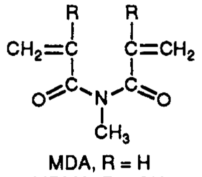
Communications to the Editor

Cyclopolymerization. 16. Anionic Cyclopolymerization of *N*-Methyldiacrylamide: 5-Membered Ring Formation through Head-to-Head and Tail-to-Tail Additions

Radical cyclopolymerizations of N-substituted dimethacrylamides (RDMA)[1–5] and diacrylamides (RDA)[6–8] have been reported. Both groups of monomers have extremely high cyclization tendencies and yield polymers with a 5-membered ring as the main repeating cyclic unit. Despite the structural similarity of the polymers formed, the reactivities of the double bonds involved in RDMA and RDA are essentially different. This can be seen from the polymerizabilities of N,N-disubstituted methacrylamides and acrylamides, which are considered to correspond to the monofunctional counterparts of RDMA and RDA, respectively. The former cannot be polymerized,[3,4,9] while the latter have a high polymerization tendency.[10] Thus, fundamental aspects for the formation of a highly cyclized polymer in radical polymerization are considered to be different for RDMA[4] and RDA.[8] Although considerable accumulated data are thus available for the radical polymerization of RDMA and RDA, especially for the former, anionic polymerization of these monomers has not been reported except for preliminary results on *N*-methyldimethacrylamide (MDMA),[2] which showed that 6-membered rings are formed as the main repeating unit in



MDA, R = H
MDMA, R = CH_3

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Table I
Anionic Polymerization of MDA at -78 °C in THF[a]

no.	time, min	convn, %	[η], dL/g
1	0.5	6.0	0.08
2	5	13.1	0.09
3	30	14.4	0.09

[a] $[M]_0 = 0.29$ mol/dm^3; $[I]_0 = 2.5 \times 10^{-2}$ mol/dm^3.

contrast to the radical polymerization. In order to see the influence of the reactivities of the double bonds involved in RDMA and RDA on their anionic polymerization and to obtain a comprehensive understanding of the cyclopolymerization behavior of these monomers, anionic cyclopolymerization of *N*-methyldiacrylamide (MDA) was undertaken. MDA is a favorable monomer for this purpose since the three possible structural units of poly-MDA, i.e., 5- and 6-membered rings and pendant uncyclized unit, can be distinguished by spectroscopic methods.[8] Therefore, the correlation between experimental conditions and the structure of the polymer formed can be studied.

MDA was prepared according to the procedure reported,[6] dried over a molecular sieve, and distilled before use under dry nitrogen. Tetrahydrofuran (THF) was purified in the usual way. Commercial t-butylmagnesium chloride (*t*-BuMgCl) solution in THF (Tokyo Kasei) was used as an initiator. Cyclic model compounds, *N*-methylsuccinimide (MSI) and *N*-methylglutarimide (MGI), were prepared according to the procedure reported.[3]

All procedures were carried out under dry nitrogen. Polymerizations were undertaken in a glass ampule with a branch. Monomer solution and catalyst solution were introduced into the main tube and the branch, respectively. After the ampule was cooled to -78 °C, both solutions were mixed together at this temperature. The moment of mixing was regarded as the time when polymerization started. After a given time, a small amount of methanol containing added hydrochloric acid was introduced to the polymerization mixture at -78 °C and the polymer was precipitated in diethyl ether.

^{1}H NMR and ^{13}C NMR spectra were taken on a JEOL JNM-GX-270 FT NMR spectrometer using dimethyl-d_6 sulfoxide (DMSO-d_6) or $CDCl_3$ as solvents and tetramethylsilane as an internal standard. Trifluoroacetic acid was added to shift the signal due to water in ^{1}H NMR measurements in DMSO-d_6. IR spectra were recorded on a Hitachi 260-30 IR spectrometer. Viscosities were measured in Ubbelohde viscometer at 30 °C in *N*,*N*-dimethylformamide (DMF).

The results of the polymerizations are summarized in Table I. Polymerization proceeds very rapidly after the monomer and catalyst solutions are mixed. However, it stops almost immediately, probably due to the side reactions which occur in the anionic polymerization of polar monomers.[11] The polymers formed are soluble in solvents such as DMF and DMSO. However, they contain a fraction insoluble in chloroform, in which poly-MDA obtained by radical polymerization is soluble.

Structural characterization of poly-MDA was carried out on the basis of the method established for poly-RDMA.[3,4] Comparison of stretching vibrations of carbonyl groups in IR spectra of several compounds including poly-MDA and cyclic model compounds i.e., MSI and MGI, leads to the conclusion that main repeating unit of poly-MDA obtained by anionic polymerization is a 5-membered ring (Figure 1). The ^{1}H NMR spectrum of poly-MDA obtained by anionic polymerization is shown in Figure 2A. It is essentially the same as that obtained by using a radical initiator (Figure 2B) except for the weak signal due to the pendant unsaturation and the absorption due to *tert*-butyl protons derived from initiator fragment. Judging from the chemical shifts of the >N-CH_3 protons of cyclic model compounds given in Table II, a weak signal at 2.92 ppm in ^{1}H NMR spectra of poly-MDA measured in DMSO-d_6 might be attributable to >N-CH_3 protons of 6-membered rings. However, the fact that ^{1}H NMR spectrum of the radically obtained polymer measured in $CDCl_3$ (Figure 2C) does not show a signal that can be attributable to >N-CH_3 protons of 6-membered rings suggests that the repeating cyclic structure of poly-MDA obtained by anionic polymerization consists almost exclusively of 5-membered rings as well as the polymers obtained by radical polymerization.[6,8] Further, the absence of 6-membered rings in poly-MDA obtained by anionic polymerization is confirmed by obtaining the ^{13}C NMR spectrum, which is illustrated for the carbonyl carbon in Figure 3 together with the spectra of cyclic model compounds.

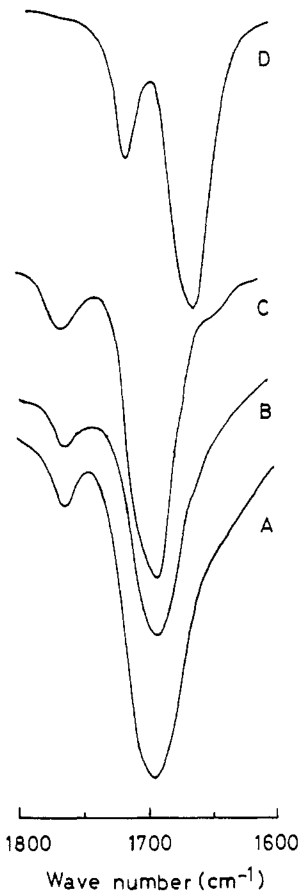

Figure 1. IR spectra of poly-MDA and cyclic model compounds: A, poly-MDA (no. 3 in Table I); B, poly-MDA obtained by radical polymerization at -78 °C,[8] C, MSI; D, MGI. Spectra A and B were measured in KBr pellet and C and D were recorded in benzene.

Table II
^{1}H NMR Chemical Shifts (δ) of >N-CH_3 Protons of Cyclic Model Compounds

solvents	MGI	MSI
DMSO-d_6	2.98	2.80
$CDCl_3$	3.13	2.99

As far as the authors' knowledge goes, this is the first report which confirms head-to-head and tail-to-tail additions in anionic polymerization. It appears that MDA has a definitely different anionic polymerization behavior from that of MDMA which yielded a 6-membered ring as the repeating cyclic structure under the same experimental conditions except for the initiator used.[2] In order to clarify

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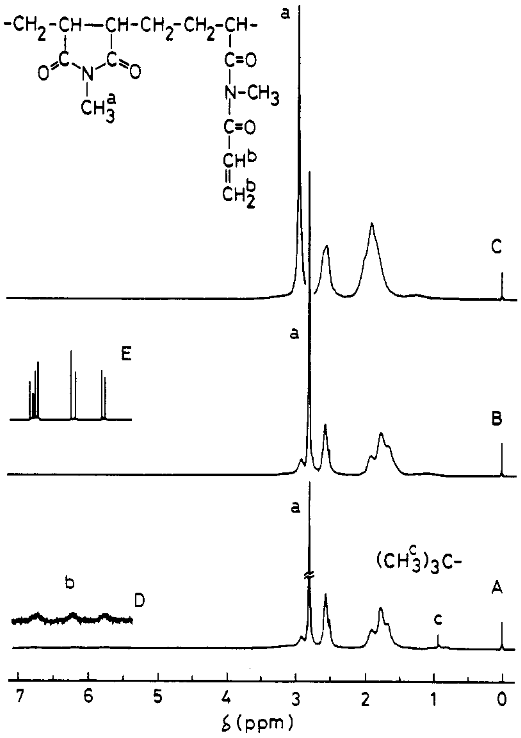

Figure 2. ^{1}H NMR spectra of poly-MDA and MDA: A, poly-MDA (no. 3 in Table I) in DMSO-d_6; B, poly-MDA obtained by radical polymerization at -78 °C[8] and recorded in DMSO-d_6; C, spectrum measured in $CDCl_3$ for the polymer of spectrum B; D, measured in increased gain for the spectrum A; E, $CH_2{=}CH$ protons of MDA in DMSO-d_6.

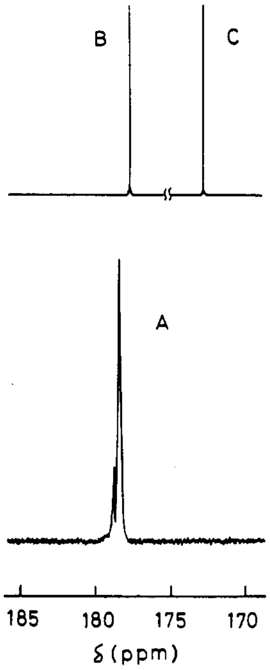

Figure 3. ^{13}C NMR spectra of carbonyl carbon in poly-MDA and cyclic model compounds: A, poly-MDA (3 in Table I); B, MSI; C, MGI measured in DMSO-d_6.

the mechanism of the 5-membered ring formation, further studies are now in progress.

Registry No. MDA, 44889-28-3; MDA (homopolymer), 30641-22-6; MSI, 1121-07-9; MGI, 25077-25-2; *tert*-butylmagnesium chloride, 677-22-5.

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Effect of Pressure on the Solid-State Structure and UV-Visible Absorption Spectra of Symmetrically Substituted Poly(di-*n*-alkylsilylenes)

The unusual and intriguing thermochromic behavior of the symmetrically substituted poly(di-*n*-alkylsilylenes) both in solution and in the solid has been well documented.[1-7] For example, a film of poly(di-*n*-hexylsilylene) (PDHS) at 46 °C shows only a strong UV absorption band centered at 316 nm, but upon cooling below 42 °C it develops an intense red-shifted band at 374 nm.[1] Under these conditions, X-ray and electron diffraction studies[7] indicate the presence of a crystalline component (phase I) having an all-trans silicon backbone together with a conformationally disordered phase (phase II). Above 42 °C the phase I structure is converted to an intermolecularly ordered phase II via a solid-state transformation. The direction of the silicon backbone chain is preserved, but two-dimensional randomization of the hexyl side chains leads to an expansion in cross-sectional area and cylindrical packing on a hexagonal lattice. The red-shifted UV absorption band that is observed below 42 °C is attributed to enhanced σ-conjugation in long sequences of trans silicon bonds.[8-10]

We now report that the 374 nm band is generated above the 42 °C transition upon subjecting a film of PDHS to pressure.[11] In Figure 1 this piezochromic effect is shown for nine values of the pressure ranging from 0.1 to 250 MPa (ca. 2500 atm). At the highest pressure the 316 nm band is almost completely replaced by the red-shifted band. When the pressure is released, the spectrum immediately reverts to the original spectrum; this is consistent with a conformational transition between an ordered and a disordered phase. The presence of an isosbestic point in the absorption spectra at different pressures indicates that the pressure-induced transition occurs between two distinct states (conformations) of the polymer and does not involve

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