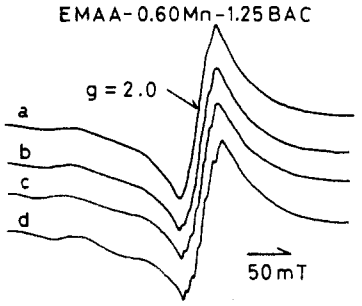

Figure 5. ESR spectral changes of the decolorized EMAA–0.60Mn–1.25BAC with exposure to air. The decolorized sample after heat treatment at 130 °C in vacuo gave spectrum a at room temperature. Its vacuum was then broken and after some aging times spectra b (6-h aging), c (78-h aging), and d (416-h aging) were obtained.

order–disorder transition near 57 °C (T_i). The ordered structure inside the ionic clusters is transformed into a disordered state above T_i. When the sample is cooled from a temperature above T_i to room temperature, the ionic clusters are in the disordered state inside but gradually reconstruct the ordered structure with a long relaxation time of about 32 days at 28 °C. In EMAA–0.60Mn–0.83BAC, T_i was about 51 °C, obtained by DSC and thermal expansion measurements. The ionic clusters are of course assemblies of the complex Mn(II) salts with BAC. It is the ordered ionic clusters but not the disordered ones that adsorb O_2 molecules selectively; this conclusion is drawn from the following facts: (1) The decolorizing of dark brown samples occurs above 70 °C, which may correspond to T_i (51 °C), as inferred from the effect of heating speed on the visible absorption measurements (see Figure 2b). (2) The amount of O_2 adsorbed chemically increases upon aging the decolorized samples at room temperature under O_2, but the dissolution of O_2 in the polymer matrix occurs only in the dark brown sample (see Figure 4). (3) We are carrying out ESR work on EMAA–xMn–yBAC. Preliminary data indicate that O_2 molecules are adsorbed at the vicinity of Mn^{2+} inside the ionic clusters.[8] Figure 5 shows ESR spectra of EMAA–0.60Mn–1.25BAC (decolorized sample) taken at room temperature after the heat treatment above 130 °C in vacuo. When the decolorized sample annealed at 130 °C in vacuo was stored at room temperature under air (O_2) atmosphere, several broad peaks, which may be ascribed to the Mn^{2+}–Mn^{2+} fine structure in the ionic aggregations,[9] became sharper and stronger, whereas the Mn^{2+}–Mn^{2+} interaction gradually decreased in magnitude. In addition, the six hyperfine line absorptions of isolated Mn^{2+} ($I = {}^5/_2$)[9] appeared. These results suggest that ordered ionic clusters are formed on storing at room temperature and that adsorption of O_2 to Mn^{2+} weakens the Mn^{2+}–Mn^{2+} interaction. Thus ESR results are fully compatible with the visible spectral variation by temperature as well as by absorbing O_2 gas.

In conclusion, this work indicates that the EMAA–Mn–BAC system selectively adsorbs O_2 gas and the adsorption site is the ordered ionic clusters formed by the complex Mn(II) ions with BAC.

Registry No. EMAA–xMn–yBAC (complex), 121231-23-0; O_2, 7782-44-7; N_2, 7727-37-9.

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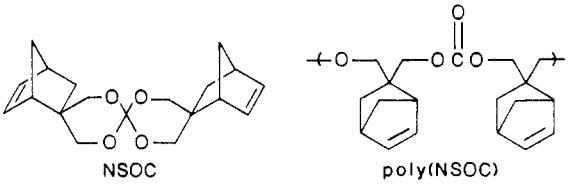
Unusual Ring-Opening Polymerization of a Spiro Orthocarbonate Containing Norbornene Moiety

Cationic polymerization of norbornene spiro orthocarbonate (NSOC) is believed to proceed according to the general polymerization mode accepted for all other six-membered spiro orthocarbonates (SOCs) (Scheme I[1]), to give poly(ether–carbonate), poly(NSOC).[2] NSOC is an



important monomer among many SOCs which show expansion in volume on polymerization[1c,3] since it has been actually used for carbon fibre composites and epoxy coatings with improved toughness and stability by reducing shrinkage stress of epoxy resin matrix.[2,4] Recently we have found, however, that NSOC polymerizes cationically along a different mechanism from Scheme 1 to afford a structurally different polymer from [poly(NSOC)], which is described in this paper.

NSOC (mp 270 °C) was treated with BF_3OEt_2 at 100 °C in chlorobenzene (100 wt %) for 24 h.[5] The polymer obtained as the methanol-insoluble fraction (yield 50%, $\bar{M}_n$ 3100, $\bar{M}_w/\bar{M}_n$ 1.75)[6] did show very reduced olefinic proton signals (to 22% of the original NSOC) in ^1H NMR as illustrated in Figure 1A,B, although IR and elemental analysis data[7] did not deny the proposed poly(ether–carbonate) structure, poly(NSOC).[8] In more than 20 experiments under various conditions the reduction of the olefinic signals was always observed. Especially, the signals decreased to only 2% under drastic conditions (with 50

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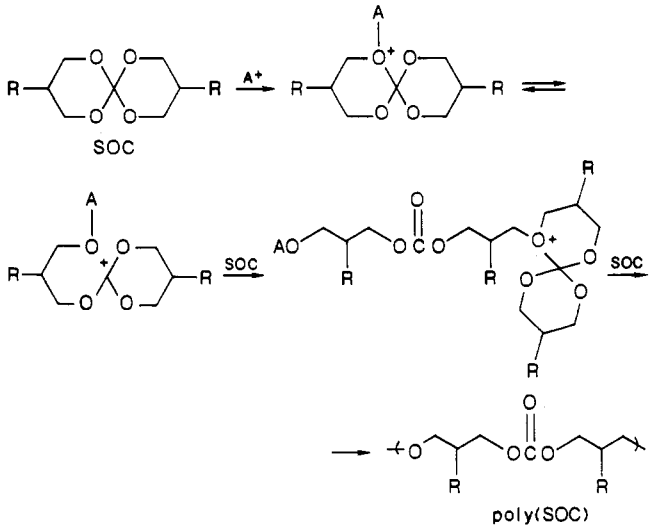
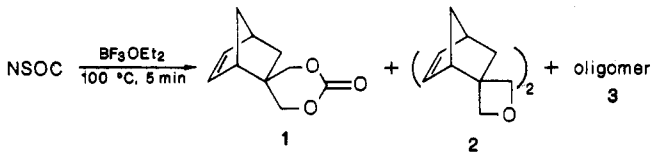
Scheme I



Scheme II



wt % solvent and 20 mol % catalyst at 100 °C for 24 h). Even at room temperature (polymerization time 30 days), the olefin content was 53%. The olefin content certainly dropped down along with increase of concentration, temperature, and amount of the catalyst. In accordance with this, both molecular weight and its distribution increased.[9] This behavior did not depend on kinds of catalyst (BF_3OEt_2, $PhCH_2\overline{S^+CH_2CH_2CH_2CH_2}SbF_6^-$, or $BF_3H_2N^nPr$), solvent (PhCl, $ClCH_2CH_2Cl$), and temperature (from room temperature, to 180 °C), though its magnitude varied. On the other hand, in the copolymerization with phenyl glycidyl ether most olefinic proton signals of NSOC similarly disappeared in the copolymer (olefin content 18%).[10] The significant decrease of the degree of unsaturation seems to indicate a polymerization involving a cyclization process.

Meanwhile, by examination of the initial stage of the polymerization, it was found that all NSOC was completely consumed in only 5 min, but no polymer appeared. The products obtained by chromatographic separation were a spirocyclic carbonate[11] (1, 54%), dimer of an oxetane[12] (2, 25%), and an oligomeric mixture (3, 21% yield, 72% olefin content) (Scheme II). Since the yield of 1 was sufficiently high (95% of theoretical yield), at least most NSOC would not undergo a polymerization via the previously accepted mechanism like Scheme I.

Then the polymerizability of 1 was examined under the same conditions (BF_3OEt_2: 5 mol %, 100 °C, PhCl: 100 wt %, 24 h). The methanol-insoluble fraction collected (25% yield, $\bar{M}_n$ 1500, M_w/M_n 2.37) was a polycarbonate that had no olefinic proton at all (Figure 1C).[12] The methanol-soluble fraction (75% yield) also had a very low olefin content (12%).

In order to confirm the special effect of the norbornene structure on the above polymerizations, the polymerizations of the following three compounds were carried out under similar conditions. Cyclohexene derivative 4 polymerized inefficiently to yield a polymer (18% yield) that had rather high olefin content (71%). Both 5 and 6 with saturated norbornene structures showed little polymerizability. Therefore, the norbornene structure plays an important role in the polymerization of both NSOC and 1.

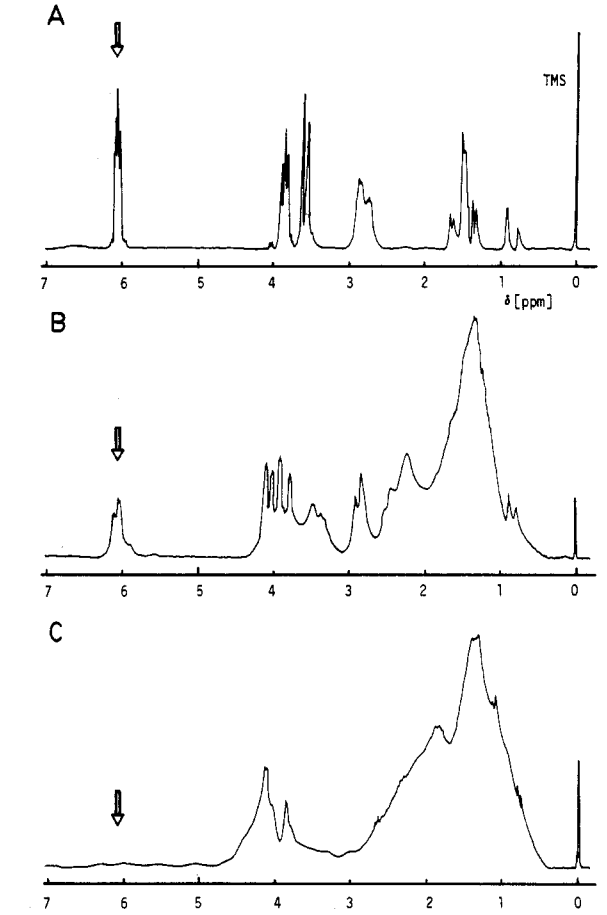
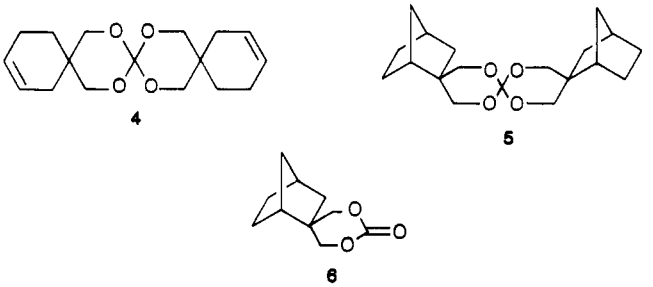


Figure 1. 100-MHz FT NMR spectra of (A) NSOC, (B) the polymer of NSOC (polymerization conditions: BF_3OEt_2, 5 mol %; PhCl, 100 wt %; 100 °C; 24 h, 26% olefin content), and (C) the polymer of 1 (same conditions as those of (B)) in $CDCl_3$. Arrows indicate the position of the olefin signals.



The disappearance of the olefin seems to take place mainly in the second stage,[13] which occurs successively after the decomposition of NSOC. Its mechanism may be explained by assuming the easy formation of a nonclassical type of carbenium ion intermediate by the assistance of the olefin group located at intramolecularly favorable position,[14,15] which obviously makes the polymer structure complicated by possible cyclization–skeleton rearrangement prior to nucleophilic attack of the monomer.[16]

Thus, in this paper we have described that the cationic polymerization of NSOC is different not only in its mode but also in the polymer structure from those believed for all other six-membered SOCs. These polymerization of NSOC is suggested to proceed via the initial rapid decomposition of NSOC followed by successive (co)polymerization of the cyclic carbonate 1 and the oxetane derivative, e.g., 2. The results are believed to provide an

important insight in studying on the origin of the good character of NSOC and in designing more useful SOCs.

Registry No. NSOC (homopolymer), 101702-62-9; NSOC, 96837-22-8.

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(5) Since NSOC was almost insoluble in PhCl, the polymerization system was initially heterogeneous but soon became homogeneous.

(6) $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were determined by GPC (THF, polystyrene standard), in which the peak was unimodal.

(7) Anal. Calcd for $C_{19}H_{24}O_4$ (found): C, 72.13 (72.35); H, 7.65 (7.95). IR (KBr) 1747 (C=O), 1257 (O—CO_2), 1105 cm^{-1} (C—O—C).

(8) The soluble part contained a similar polymer with a lower $\bar{M}_n$ and some oligomers.

(9) This can be accounted for by the occurrence of a post reaction between polymers formed during the polymerization. In fact, NSOC polymer with 35% olefin content was converted to a polymer with 14% olefin content and increased $\bar{M}_w/\bar{M}_n$ based on polymodal GPC, accompanying gel polymer (16%), when it was treated under the same conditions as that in the polymerization.

(10) Takata, T.; Kitazawa, K.; Amachi, K.; Endo, T. *Polym. Prepr. Jpn.* **1987**, *36*, 1349. A 2:8 mixture (NSOC:phenyl glycidyl ether) was heated with $PhCH_2\overline{S^+CH_2CH_2CH_2CH_2SbF_6^-}$ (5 mol %) in bulk at 120 °C for 5 h. Methanol-insoluble copolymer was obtained in 31% yield (unimodal GPC peak, $\bar{M}_n$ 2700, $\bar{M}_w/\bar{M}_n$ 1.93, segment ratio 23:77).

(11) Mp 92–94 °C from *n*-hexane; IR (KBr) 1765, 1730, 1180, 1090 cm^{-1}; ^{13}C NMR ($CDCl_3$) 138.9, 133.6 ppm (C=C). Anal. Calcd for $C_{10}H_{12}O_3$ (found): C, 66.65 (66.90); H, 6.71 (6.68).

(12) IR (neat) 1140, 1120, 1070 cm^{-1}; mass, m/z 272 (M^+). Anal. Calcd for $C_9H_{12}O$ (found): C, 79.36 (79.04); H, 8.88 (8.98).

(13) No gel polymer was obtained in any polymerization of NSOC. From the results of the polymer reaction,[9] decrease of the olefin content due to the post reaction between the polymers formed might not be the major route.

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(15) For the polymerization of 1 the following scheme is proposed

(16) In fact, it is quite difficult to determine the exact structures of the polymers of both NSOC and 1, because in ^{13}C NMR a lot of signals corresponding to methine and methylene carbons appeared in a region from 50 to 30 ppm.

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