Macromolecules **2003,** *36,* 1433−1435

Solid-State Polymerization of Dibenzofulvene Leading to a Copolymer with Oxygen

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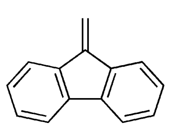
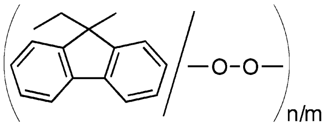
Received October 31, 2002
Revised Manuscript Received January 18, 2003

Introduction. Solid-state polymerization is an efficient method in controlling polymer structure. Several diyne and diene monomers undergo solid-state polymerization, leading to polymers with controlled chemical and stereostructures.[1,2] However, there has been no clear examples of solid-state polymerization of vinyl monomers except for the reactions using solid matrices (inclusion polymerization).[3] In this study, we found that dibenzofulvene (DBF), a vinyl monomer, copolymerizes with oxygen in the solid state to give a polymer with structure **1**. We recently reported[4] that DBF is a highly reactive monomer in vinyl homopolymerization in solution despite its bulky structure resembling 1,1-diphenylethylene,[5] which does not homopolymerize. DBF is also reactive in the solid-state polymerization.



DBF



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Octadecyl sorbate forms an alternating copolymer with oxygen under light irradiation in the solid state.[6] Tetrakis(ethoxycarbonyl)quinodimethane also leads to a copolymer with oxygen in the solid state.[7]

Experimental Section. a. Materials. DBF was synthesized from 9-hydroxymethylfluorene by the reaction in a methanol solution containing KOH according to the literature.[8,9] The crude monomer was extracted with hexane from the reaction mixture (purity >98% by ^{1}H NMR). DBF solid for the polymerization was obtained by two methods: (i) removal of solvent from the hexane solution of crude product using a rotary evaporator to give fine powdery crystals (mp 52.6 °C (DSC)) or (ii) recrystallization from a hexane solution at −20 °C under a N$_2$ atmosphere to give needlelike crystals (mp 52.8 °C (DSC)). The obtained solid-state monomer was stored under a N$_2$ atmosphere in the dark at −20 °C until it was used for polymerization. The purity of O$_2$ gas used for polymerization was 99.6%.

b. Polymerization. As a typical example, the procedure for run 1 in Table 1 is described. The DBF monomer crystal (976 mg) was transferred to a 100 mL glass ampule under a N$_2$ atmosphere in the dark. The ampule was flushed with air and sealed with a septum. The reaction system was allowed to stand for 24 h on the top of the lab bench under four 32 W fluorescent lamps built in the ceiling ca. 2 m from the benchtop. CHCl$_3$ (5 mL) was added to the reaction mixture, and the insoluble-part was collected by filtration and dried under vacuum (69 mg). The CHCl$_3$ solution was poured into hexane (100 mL), and the CHCl$_3$-soluble, hexane-insoluble part was collected by filtration and dried in a vacuum (322 mg). The CHCl$_3$-soluble, hexane-soluble part was recovered by removing the solvent. The hexane-soluble part was mostly monomer as indicated by ^{1}H NMR analysis.

Results and Discussion. The conditions and results of copolymerization are shown in Table 1. Upon standing in the flask under air or O$_2$ atmosphere, DBF crystals gave a polymer. The monomer crystals became slightly yellow during the reaction, but there was no change in the apparent state of the solid material, indicating that the reaction took place in the solid state. The reaction under pure O$_2$ resulted in higher polymer yield (runs 1 and 2) while under N$_2$ atmosphere, no reaction was confirmed (run 3). These results indicate that oxygen, as a part of air or a pure purge gas, is involved in the polymerization. As discussed later, the products were a copolymer consisting of DBF and −O−O− units.

The polymerization products contained the CHCl$_3$-insoluble part in all cases; the CHCl$_3$-soluble, hexane-insoluble part was mainly characterized. The CHCl$_3$-insoluble and soluble parts showed very similar IR and Raman spectra (Supporting Information), suggesting that they have the same chemical structure and the insoluble part may have a higher molecular weight.

The reactions using recrystallized monomer and as-evaporated monomer both led to a polymer under air (runs 1 and 4). In the polymerization under air, the polymer yield increased by extending the reaction time from 24 to 96 h, but further extension of reaction time did not have a clear effect on polymer yield (runs 1, 5, 7, and 9). The polymerization occurred in the dark as well as in the presence of ambient light (runs 5−8). The ambient light seems to have little effect on the polymerization behavior. The observed polymerization activity in the dark is in contrast to the fact that sunlight or UV irradiation is necessary for the octadecyl sorbate−O$_2$ copolymerization system.[6] The polymerization did not occur at 0 °C or lower temperatures.

The polymer structure was characterized by MALDI-MS and ^{1}H NMR spectra. The mass numbers of the peaks observed in the MALDI-MS spectra of the CHCl$_3$-soluble polymer from run 1 in Table 1 corresponded approximately to the molecular weights of a structure consisting of DBF units and oxygen atoms (Figure 1). This indicates that oxygen was incorporated into the polymer chain. The slight differences between the observed and calculated mass numbers may be due to the limited spectral resolution and intensity. It was

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10.1021/ma025792r CCC: $25.00

Table 1. Solid-State Copolymerization of DBF with Oxygen[a]

						hexane-insoluble products			
						$CHCl_3$-soluble part			$CHCl_3$-insoluble part
run	monomer crystals[b]	purge gas	time (h)	light[c]	temp (°C)	yield[d] (%)	$M_n{}^e \times 10^{-3}$	$M_w/M_n{}^e$	yield (%)
1	i	air	24	ambient	ca. 23	33	13.1	1.58	7
2	i	O_2	24	ambient	ca. 23	69	9.5	1.79	8
3	ii	N_2	24	ambient	ca. 23	0			
4	ii	air	24	ambient	ca. 23	29	7.8	1.68	2
5	i	air	96	ambient	ca. 23	48	8.7	2.02	13
6	i	air	96	dark	ca. 23	53	10.6	1.78	9
7	i	air	168	ambient	ca. 23	49	7.6	1.80	14
8	i	air	168	dark	ca. 23	61	9.0	1.99	9
9	i	air	336	ambient	ca. 23	53	6.8	1.66	9
10	i	air	24	ambient	0	0			
11	i	air	24	ambient	−20	0			

[a] Monomer 0.5−1g. [b] i: monomer obtained by simple removal solvent; ii: monomer obtained by recrystallation. See Experimental Section. a. Materials for details. [c] The reactions were carried out on the top of the lab bench under four 32 W fluorescent lamps built in the ceiling ca. 2 m from the bench top (abmient light) or in the dark. [d] Based on the weights of the product and DBF monomer in feed. [e] Determined by GPC using a rectangular light-scattering information obtained with a Wyatt DAWN-E detector.

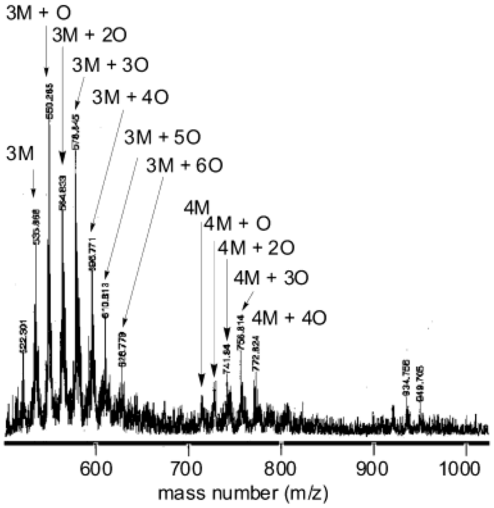

Figure 1. MALDI-mass spectrum of the polymer from run 1 in Table 1 ($CHCl_3$-soluble part) obtained using dithranol as a matrix. The nM + mO notation means the molecular weight of a species consisting of n DBF units and m oxygen atoms.

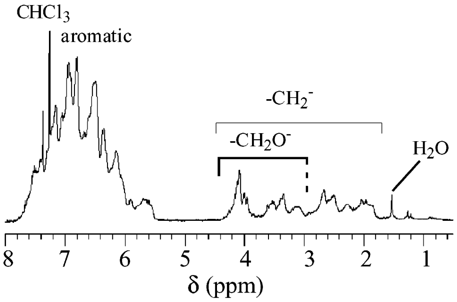

Figure 2. ^{1}H NMR of the polymer from run 1 in Table 1 ($CHCl_3$-soluble part) (500 MHz, $CDCl_3$, room temperature).

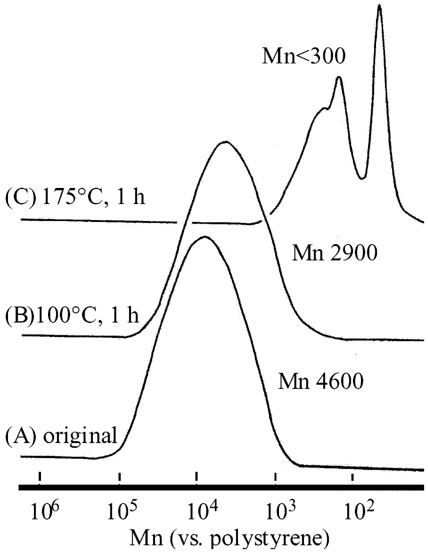

Figure 3. SEC curves of the polymer from run 1 in Table 1 ($CHCl_3$-soluble part): before pyrolysis (A), after heat treatment at 100 °C for 1 h (B), or at 175 °C for 1 h (C).

difficult to observe clear peaks in the higher mass range than shown in Figure 1, implying that the polymer has a relatively weak main-chain bonding and readily decomposes into oligomeric fragments under the measurement conditions in this study. In addition, the existence of mass peaks corresponding to the multiples of DBF molecular weight indicates the presence of DBF homopolymeric sequences in the copolymer.

The NMR spectrum of the polymer from run 5 of Table 1 indicates the complete consumption of vinyl group of DBF,[10] meaning that DBF reacted in the polymerization through opening of the vinyl group (Figure 2). The peaks in the range of 1.6−4.2 ppm were assigned to $-CH_2-$ protons because the intensity ratio of the peaks in this range to the peaks in the aromatic region was 2:8. This supports that DBF units in the polymer exist as vinyl monomeric unit without isomerization. The relatively wide $-CH_2-$ peak shift range is in contrast to the fact that poly(DBF) prepared by anionic polymerization with 9-fluorenyllthium having a vinyl polymer structure shows its methylene signals mainly in the range of 2−3 ppm. The $-CH_2-$ peaks in the range of ca. 3−4.2 ppm in Figure 2 may be ascribed to $-CH_2-$ groups next to an oxygen atom because the relative intensity of peaks in this range in the entire $-CH_2-$ peak intensity approximately coincides with the $-O-O-$ content discussed later.

Pyrolysis experiments also provide structural information. When the powder sample of the polymer from run 1 in Table 1 ($CHCl_3$-soluble part) was heated at 100 °C for 1 h in a drying oven under air, molecular weight[11] of the polymer decreased from 4.6×10^3 to 2.9×10^3. Upon heating of the same polymer (powder) at 175 °C for 1 h, molecular weight decreased to less than 300 (oligomers). These results indicate that the polymer has thermally degradable linkages in the main chain that are reasonably assumed to be −O−O− bondings. The presence of −O−O− bondings was supported by FT-Raman spectra indicating a peak at 1115 cm^{-1} (Supporting Information). The analytical results described so far strongly support that the copolymers obtained in this work has structure **1** although the chain terminal structure is not yet clear.

The content of −O−O− bonding in the main chain was estimated by elemental analysis of the polymers from runs 1 and 2 ($CHCl_3$-soluble part) in Table 1. The elemental compositions were C, 82.84; H, 5.10 (run 1) and C, 80.3; H, 5.01 (run 2), corresponding to the ratios of [DBF unit] to the [−O−O−] unit, 1.0/0.70 and 1.0/0.86, respectively, assuming structure **1**.[12] On the basis of these numbers along with the results of MALDI-MS analyses, the polymers may have mixed −DBF−O−O− alternating and DBF homopolymeric sequences. The fact that a higher O_2 pressure resulted in a higher −O−O− unit content implies that polymer structure could be controlled in a wider range by regulating O_2 pressure.

Although the details of the reaction mechanism are not currently clear, the following points may be noted. First, M_n of the products ($CHCl_3$-soluble part) tended to decrease by extending the reaction time while polymer yield only slightly increased after 96 h (runs 5, 7, and 9). This suggests that main-chain scission competes with the polymerization. Second, no homopolymeric DBF sequences or a copolymer was formed under N_2 (run 3), suggesting that the homopolymeric sequence may be formed by radical mechanism with O_2 as an initiator. In addition, the reaction using pure O_2 afforded a polymer with a higher −O−O− content in a much higher polymer yield than the one using air under the same conditions (runs 1 and 2). This along with the second point may imply that incorporation of O_2 into the polymer chain more readily takes place than the growth of homopolymeric DBF sequences. The incorporation of O_2 may occur through radical coupling of O_2 with growing homopolymeric or copolymeric DBF radical as well as radical addition of O_2 to DBF monomer to give a DBF radical.

We have shown that DBF copolymerizes in the solid state with oxygen in the air to afford a polymer consisting of DBF units and peroxy units. Copolymers of vinyl monomers with oxygen giving alternating −O−O− and vinyl monomeric units have been prepared by solution polymerization, but the existing examples required cobalt initiators.[13,14] In contrast to the existing examples,[6,7,13,14] the present polymerization systems do not require added initiators, light, or heat. This demonstrates the high reactivity of DBF not only in the vinyl polymerization in solution[4] but also in the solid-state reaction. Studies are under way to understand the reaction mechanism and the nature of growing species and to find parallels to the present system.

Acknowledgment. We thank Prof. A. Matsumoto (Osaka City University, Japan) for valuable discussions. Mr. A. Nara (ThermoNicolet, Japan) is acknowledged for the FT-Raman measurement.

Supporting Information Available: FT-Raman and IR spectra of $CHCl_3$-insoluble and -soluble polymers from run 1 in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The chemical shift of vinyl group of DBF is 6.08 ppm ($CDCl_3$, room temperature).[4]

(11) Determined by SEC vs standard polystyrenes.

(12) The −O−O− contents were calculated assuming that the samples consist only of C, H, and O. For structure **1**, the H contents found in the elemental analysis were in excess by ca. 0.1−0.2%. The analytical values were corrected on the basis of the assumption that the excess H contents were due to water contained in the sample.

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MA025792R