

The First Polycondensation through a Free Radical Chain Process

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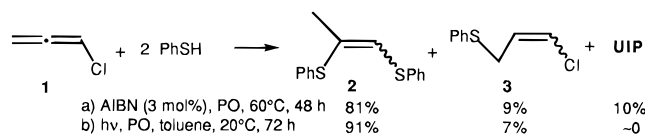
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Received January 21, 1997

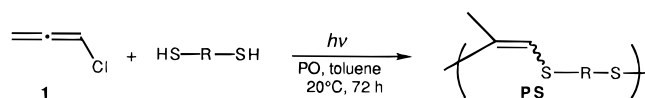
The free radical chain reaction is one of the most important polymerization processes due to its practical advantages, e.g., its susceptibility to water much lower than that of ionic polymerization. The free radical process has been applied only to addition polymerization and polyaddition. Recent development of free radical ring-opening polymerization¹ has largely expanded the possibility of ring-opening polymerizations which have been limited to ionic process.² Meanwhile, polycondensations usually proceed with an ionic mechanism via an acid- or base-catalyzed reaction,³ in addition to those involving intervention of organometallic intermediates.⁴ However, to the best of our knowledge, there has been no example of polycondensation through a free radical chain process. Provided polycondensation through a free radical chain process could occur, a new entry to polymer synthesis would be opened and the availability of polycondensation as useful synthetic method would be enlarged. During our extensive study on polymerization of allenes and their homologues as vinyl-functionalized vinyl monomers,^{5–7} we have recently found the first example of polycondensation through free radical chain process, which is disclosed in this paper.

Bisallenenes react with dithiols to afford corresponding polyaddition products in high yields under typical radical conditions via selective formation of central carbon–sulfur bond.⁶ Radical

Scheme 1



Scheme 2



addition of thiol to allene as a model reaction similarly proceeds to give corresponding 1:1 adduct in a certain selectivity.^{6,8} When the radical addition of thiophenol to chloroallene (1) (1:1 ratio) was carried out, we obtained a few products including 1,2-bis(phenylthio)propene (2, 15%) and 1-chloro-2-phenylthiopropene (11%, a formal 1:1 adduct) produced by central carbon attack of sulfur.⁹ We noticed the formation of 2, because it could be emerged presumably through an elimination of hydrogen chloride from the corresponding 1:2 adduct. To scavenge the hydrogen chloride evolved during the reaction, propylene oxide (PO) was added to the reaction system to increase the yield of 2 to 44%. Further, use of 2 mol of thiophenol enhanced the yield up to 81%, but another 1:1 adduct, 1-chloro-3-phenylthiopropene (3), was still produced in 9% yield in addition to 10% of unidentified product (UIP) (Scheme 1). Therefore photo-initiated radical reaction¹⁰ was examined to elevate the product selectivity by lowering the temperature from 60 to 20 °C. As a result, the yields of 2 and 3 were 91 and 7%, respectively, whereas the formation of UIP was almost suppressed.

The polymerization of 1 and aromatic dithiols 4–6 was conducted at 20 °C for 72 h in toluene under photoirradiation (Scheme 2, Table 1). The usual workup gave a polymeric product of which structure was determined mainly by the NMR spectra as the polymer formed by polycondensation. Typical ¹H NMR spectrum of the polymer formed by polycondensation. Typical ¹H NMR spectrum of the polymer PS is shown in Figure 1 (top). The simple signal pattern of the spectrum indicated that the polymer presumably consists only of 1,2-dithiopropene unit, while the regioisomeric ratio of *cis* and *trans* is nearly 1:1. The ¹³C NMR spectrum supported the proposed structure (Figure 1). The selected results of the polymerizations under varying conditions are summarized in Table 1.

The polymerization of 1 and 4 was carried out under the conditions same as those of Scheme 1a (Table 1, run 1) and gave only 12% yield of polymer with *M*_n 1300 (peak top value) which was roughly equal to *M*_n calculated from the product ratio of Scheme 1a. In the polymerization under the photoirradiation at 60 °C (run 2), the yield increased to 24%, although *M*_n was fairly low. However, at 20 °C the yield increased to 37% (run 3). With prolonged reaction (run 4), the polymer with *M*_n 2700 was obtained in 71% yield. It was found that use of dithiol in slight excess of up to 1.2 equiv enhances both the yield and molecular weight (runs 5–8). Further lowering of the reaction temperature (7 °C) affected the results (run 10) little. Decrease in concentration gave a little better yield and higher *M*_n presumably because of the reduced viscosity of the polymerization system (run 11).

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(9) This result was consistent with that of Pasto *et al.*,^{8a} although they reported no details such as yield of the products. Other products: abnormal 1:1 adduct, 1-chloro-3-phenylthiopropene (6%), and 1:2 adduct, 1,2-bis(phenylthio)-2-chloropropane (19%).

(10) Reaction conditions: Pyrex filter, toluene, 20 °C, 72 h, PO (2 equiv), and irradiation with a 400 W high-pressure mercury lamp.

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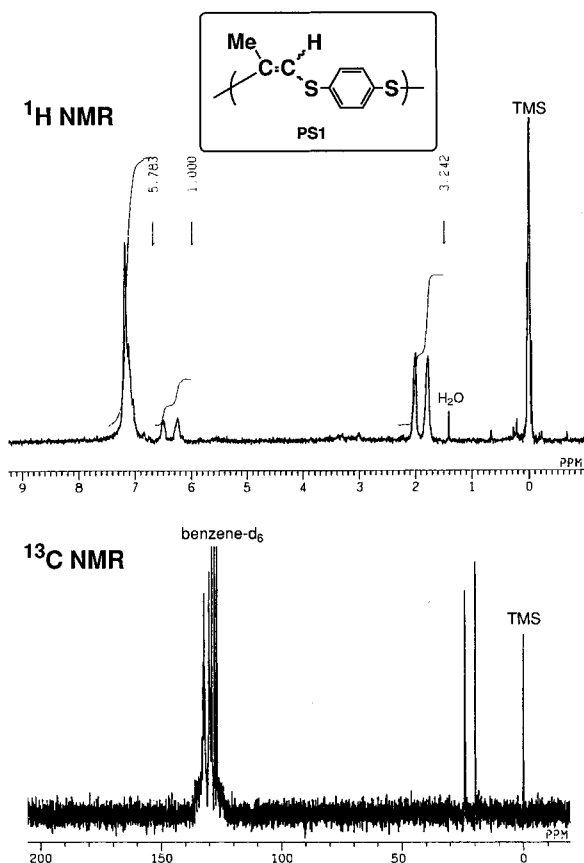
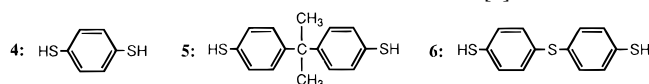


Figure 1. ^1H (CDCl_3) and ^{13}C NMR (benzene- d_6) spectra of polymer (PS1) prepared by free radical polycondensation of **1** and **4** at 20 °C under photoirradiation.

Table 1. Free Radical Polycondensation of Haloallenes and Dithiols^a

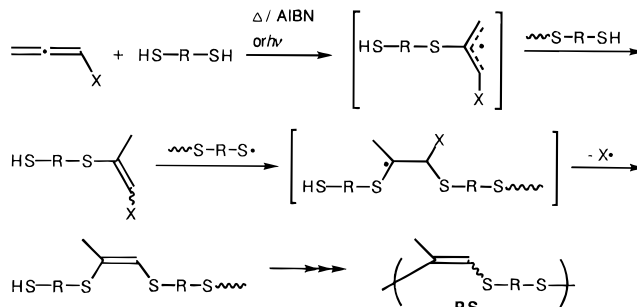
run	allene	dithiol ^b	molar ratio of allene/dithiol	temp (°C)	time (h)	polymer (PS)			
						yield (%) ^c	M_n^d	M_w/M_n^d	
1 ^e	1	4	1.1	60	48	PS1	12	1300	ND ^f
2	1	4	1.1	60	58	PS1	24	450	5.78
3	1	4	1.1	20	48	PS1	37	1500	2.72
4	1	4	1.1	20	72	PS1	71	2700	2.52
5	1	5	1.0	20	72	PS2	40	5000	1.81
6	1	5	1.1	20	72	PS2	45	5900	1.94
7	1	5	1.2	20	72	PS2	57	5900	1.64
8	1	5	1.3	20	72	PS2	42	6000	1.83
9	1	5	1.5	20	72	PS2	34	4700	1.42
10	1	5	1.1	7	72	PS2	44	5600	1.79
11 ^g	1	5	1.1	20	72	PS2	63	8300	2.15
12	1	6	1.1	20	72	PS3	85	4600	2.01
13	2	4	1.1	20	72	PS1	94	6400	3.84
14	2	5	1.2	20	72	PS2	58	5800	2.63

^a Polymerization conditions: concentration, 0.6 M in toluene; photoirradiation by a 400 W high-pressure mercury lamp in a pyrex tube. ^b Abbreviations of the dithiols are shown below. ^c Yield of cyclohexane-insoluble polymer for **4** and yield of ether-insoluble polymer for **5** and **6**. ^d Estimated by GPC (eluent, tetrahydrofuran, polystyrene standards). ^e The polymerization was carried out under the conditions shown in Scheme 1. ^f Not determined. ^g $[\text{I}] = 0.15 \text{ M}$.



Without photoirradiation or 2,2'-azobisisobutyronitrile (AIBN), no reaction took place at all; whereas, equimolar TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) added to the reaction system also suppressed the reaction completely. These results evidently suggest the free radical chain reaction. In the plausible mechanism (Scheme 3), either a radical species formed from radical initiator abstracts hydrogen of the thiol group or the thiol

Scheme 3



photochemically dissociates to give thiyl radical. The polycondensation mainly proceeds via initial attack of the thiyl radical at central carbon of **1** and subsequent attack of the resulting thiyl radical at the halogen-bonded carbon via anti-Markovnikov mode leading to α -thioradical¹¹ from which halogen radical is eliminated to afford 1,2-dithiopropene unit.

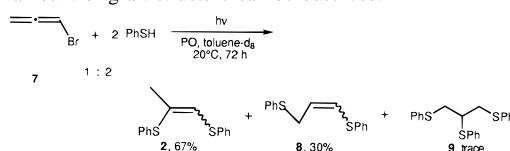
Use of excess amount of **1** (1.1 equiv) results in enhanced yield and molecular weight and use of a larger excess of **1** (~1.5 equiv) does not affect them as seriously, unlike usual polycondensation (Table 1), clearly suggesting that the second addition of thiyl radical is somewhat faster than the first one. This would be confirmed from the fact that only 65% of **1** was exhausted while 100% of thiophenol was consumed, when the addition reaction was carried out in 1:1 ratio (AIBN, 60 °C). Attack of thiyl radical at terminal carbon of **1** should result in a termination reaction from the results of the model reaction (Scheme 1). Meanwhile, due to the greater leaving ability of the Br radical, bromoallene (**7**) was employed instead of **1**.¹² Table 1 (runs 13 and 14) indicates that use of **7** causes certain increase in yield and molecular weight,^{13,14} indicating some favorable effect of the replacement of Cl with Br.

Thus, the above-mentioned results unambiguously suggest that this type of novel polycondensation through free radical chain process can be categorized as an addition–condensation. It should be of great significance to establish the first “radical polycondensation”, and some excellent molecular designs based on the results of this study will provide further useful examples to develop the new polymerization “radical polycondensation”.

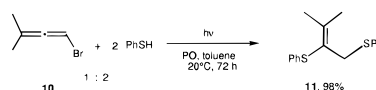
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(11) A broad signal appearing around 3.5 ppm in the ^1H NMR spectrum may be due to the methylene signal of the polymer unit formed by the terminal addition of thiol to **1**.

(12) The structure of the polymer from **7** is not so simple in comparison with that from **1**: the ^1H NMR indicates contamination of a few units different from the 1,2-diarylthiopropene unit. This is in good accordance with the model reaction using thiophenol. Rate of terminal carbon attack of thiyl radical (>30%, **8** + **9**) is much higher than that of **1** (7%): the product formed by the terminal carbon attack can further react with thiyl radical to yield **8**. Therefore, the terminal carbon attack does not result in termination unlike the case of **1**: the two main chain structures including a small amount of graft structure can be observed.



(13) To suppress the terminal carbon attack, 1-bromo-3-methyl-1,2-butadiene (**10**) was used under the same conditions as Scheme 2. However, low molecular weight polymer was obtained (74% yield, M_n 820, M_w/M_n 2.09). Unlike the radical addition of thiol to 3-methyl-1,2-butadiene yielding 1,2-adduct via the central carbon attack,¹⁴ the polymerization would proceed through initial attack of thiyl radical at the bromo-substituted terminal carbon, because the polymer is suggested to have isopropylidene moiety by the model reaction, in which a different type of 1:2 adduct **11** is selectively formed.



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