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Radical Polymerization of Alkoxyallenes

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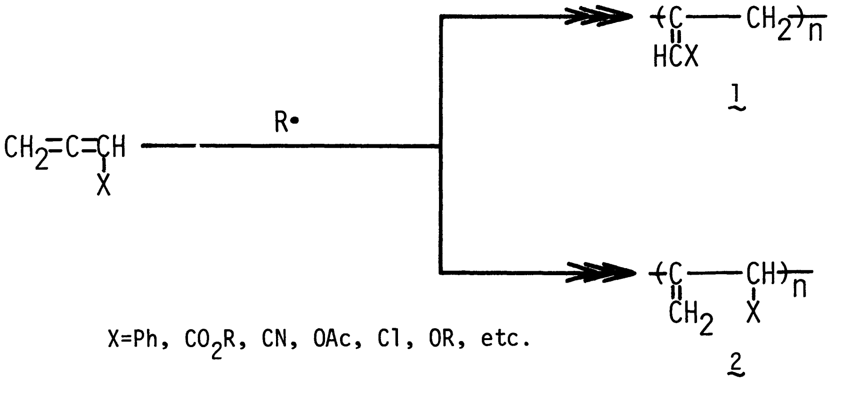
The radical polymerizations of methoxyallene and phenoxyallene were carried out to obtain the polymers which consisted of two kinds of units polymerized by 1,2- and 2,3-double bonds of allenes in both cases.

The radical polymerization of a variety of vinyl monomers has been extensively reported and also played an important role as polymeric materials. However, functional groups substituted allenes, that another methylene carbon is bonded to β-carbon of vinyl monomers, have been hardly regarded as candidates for radical monomers,[1)] although these derivatives have been successfully applied to organic synthesis.[2)]

The radical polymerization of these substituted allenes arouses interest both in the polymerization chemistry and the materialization. Thus, in the polymerization chemistry, a question is raised about the reaction position of allene monomer which leads the polymer **1** or **2**, depending on the substituent X of allenes (Eq. 1). In the materialization, the polymers **1** and **2** are expected to be very attractive as one of the reactive polymers containing exo-methylene groups.

Now we wish to report the radical polymerization of methoxy- (X=OMe, **3**)[3)] and phenoxyallenes (X=OPh, **4**), and demonstrate that the allenyl compounds (e.g. alkoxyallenes) have a good ability of radical polymerization, although the corresponding vinyl analogs (e.g. vinyl ethers) can not polymerize by radical initiation.

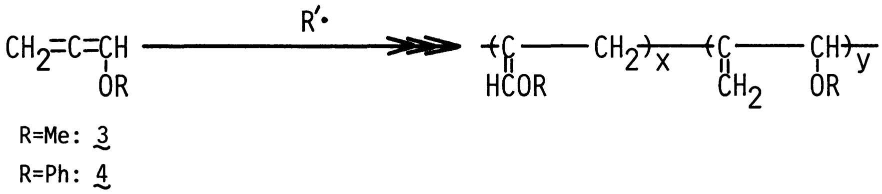


(1)

The requisite methoxy- (**3**) and phenoxyallene (**4**) were prepared by the isomerization of the corresponding propargyl ethers with potassium t-butoxide according to the reported procedure.4,5) **3** and **4** were polymerized in the presence of azobis(isobutyronitrile) (AIBN), benzoylperoxide (BPO), t-butylperoxy-3,5,5-trimethylhexanoate (TBP355), and di-t-butylperoxide (DTBP) as a radical initiator in bulk at 60-120 °C. The soluble polymers were purified by dissolution in dichloromethane, followed by precipitation in hexane.6) The results are summarized in Table 1.

Inspection of the results in the table reveals some characteristic features of the polymerization of **3** and **4**. (1) **3** and **4** can polymerize at 60-120 °C, though polymerization of **3** gives a cross-linked polymer at temperature higher than 100 °C.7) (2) **4** is more reactive in polymerization than **3** in the temperature range of this experiment. (3) The average molecular weight of the polymer obtained from **4** is generally heigher than that of **3**.

The IR spectra of both the polymers obtained from **3** and **4** showed the absorptions at 1680-1675 cm^{-1} and 1230-1220 cm^{-1} characteristic of a vinyl ether, and also the absorptions at 1640-1675 cm^{-1} and 990-980 cm^{-1} attributable to an exo-methylene. In the ^1H NMR spectra, two kinds of signals assignable to vinyl protons appeared at δ 5.0-5.3 and 5.9-6.0 ppm. From these spectral data, both polymers obtained from **3** and **4** consist of the structure units **1** and **2**, which were formed by the polymerization of 1,2- and 2,3-double bonds of allenes, respectively (Eq. 2).8) Concerning the content of the units **1** and **2** (x and y in Table 1), the value of x tends to decrease with a polymerization temperature in the case of methoxyallene **3**, while in the case of phenoxyallene **4**, the value of X is always larger independently of polymerization temperature; the reason is not clear.



$$CH_2{=}C{=}\underset{OR}{CH} \xrightarrow{R'\cdot} \left(\underset{\underset{HCOR}{\|}}{C} - CH_2\right)_x \left(\underset{\underset{CH_2}{\|}}{C} - \underset{OR}{CH}\right)_y \qquad (2)$$

R=Me: **3**
R=Ph: **4**

In summary, the present work has demonstrated that allene derivatives can be attractive compounds as reactive monomers. Thus, alkoxyallenes, in which another methylene carbon is bonded to vinyl ethers, have a good ability of radical polymerization, although vinyl ethers can not polymerize by radical initiation. Further works on the polymerization of allene derivatives as well as applications of the obtained allene polymers as functional materials are in progress in our laboratory.

Table 1. Radical Polymerization of **3** and **4**

Monomer	Radical initiator[a]	Temp °C	Time h	Yield / % I[b]	Yield / % II[c]	Yield / % Total	Polymer composition / mol%[d] x	Polymer composition / mol%[d] y
3	AIBN	60	50	9	50	59	70	30
	BPO	80	24	10[g]	39	49	47	53
	TBP355[e]	100	41	15(35)[f]	33	83	33	67
	DTBP	110	41	6(39)[f]	55	100	-	-
4	AIBN	60	46	43[h]	48	91	87	13
	BPO	80	47	36	56	92	73	27
	TBP355	100	47	45	55	100	75	25
	DTBP	120	46	43	57	100	91	9

a) 3 mol%. b) Insoluble polymer in hexane. c) Soluble polymer in hexane. d) Estimated by ^{1}H NMR analysis. e) t-Butylperoxy-3,5,5-trimethylhexanoate. f) Gel polymer. g) $\overline{\mathrm{M}}\mathrm{n}$=3500 based on polystyrene (GPC). h) $\overline{\mathrm{M}}\mathrm{n}$=7100 based on polystyrene (GPC).

References

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3) For the polymerization of methoxyallene by transition-metal catalysts, see: M. G.-Moazzam and T. L. Jacobs, J. Polym. Sci., Polym. Chem. Ed., 16, 615 (1978).

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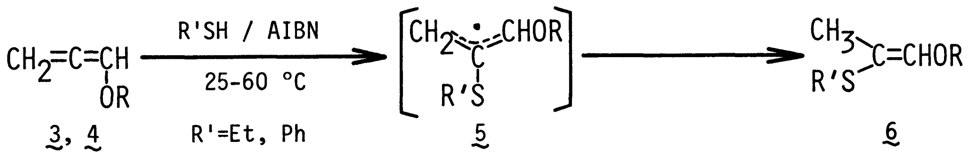
6) In the case of methoxyallene **3**, the soluble polymers were isolated by dissolution in dichloromethane, followed by precipitation in hexane containing a small amount of diphenylamine as a radical and cationic inhibitor, since the soluble polymers were converted into gel polymers on the glass surface during precipitation in the absence of inhibitor.

7) Even at 100-110 °C, the only soluble polymers could be obtained by the solution polymerization in chlorobenzene (total yield 78-90%).

8) We carried out the reaction of 3 and 4 with thiols in the presence of AIBN in order to guess the orientation of the propagating radical addition in polymerization. Thus, the reaction was carried out at 25 °C (PhSH)[9] or 60 °C (EtSH) in a sealed tube to obtain quantitatively the sole product 6 in each case, which is formed by the attack of thiyl radical to C_2 of allenes.[10,11] Similarly to above results, the propagating radical is seemed to attack also C_2 of allenes in polymerization assuming that the propagating radical had a character similar to that of thiyl radical. The fact that two kinds of units are formed in polymerization in contrast to the formation of the single product 6 in the thiyl radical addition is considered to originate from the difference between the mechanism of the radical addition to another allene monomer and that of the hydrogen radical abstraction of 5. A detailed study on polymerization mechanism is currently under way.



9) This reaction is thought to take place with radical chain mechanism even at 25 °C because the reaction was inhibited in the presence of dinitrobenzene (1 equiv. to thiophenol) as a radical inhibitor. Moreover the acid catalyzed addition of thiophenol to 3 is known to give a different product: R. W. Hoffmann and B. Kemper, Tetrahedron Lett., 1981, 5263.

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11) The boiling point and ^{1}H NMR data ($CDCl_3$, TMS) of 6 are as follows: 6a (R=Me, R'=Ph): 66 °C/0.2 mmHg; δ 1.85 and 1.89 (2s, 3H), 3.73 (s, 3H), 6.58 (m, 1H), 7.28 (bs, 5H). 6b (R=Me, R'=Et): 40 °C/5 mmHg; δ 1.14 (t, J=6.6 Hz, 3H), 1.81 and 1.83 (2s, 3H), 2.48 (q, J=6.6 Hz, 2H), 3.52 (s, 3H), 6.28 (m, 1H). 6c (R=Ph, R'=Ph): 105 °C/0.16 mmHg; δ 1.86 and 2.02 (2s, 3H), 6.87-7.57 (m, 11H).

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