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Radical Polymerization Behavior of Phenylallene. Synthesis of Functional Polymer Containing Styryl Moiety on the Backbone

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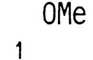
Radical homopolymerization of phenylallene (PA) and copolymerization of PA with some vinyl monomers were described. PA polymerized selectively by the terminal double bond of allene both in the homopolymerization and the copolymerization. The radical reaction of PA with thiophenol was also carried out as a model reaction of the polymerization to discuss the polymerization process of PA.

Although the radical polymerization of a broad variety of vinyl monomers have been extensively reported, very little work has been done on the radical polymerization of allene derivatives which are regarded as vinyl monomers bonded to another reactive methylene carbon. Allene derivatives and their polymers are expected to serve as functional monomers and polymers containing the reactive methylidene group, respectively. Recently, we have reported that methoxyallene (1), phenoxyallene (2),[1)] and allenyl glycidyl ether (3)[2)] show a good ability of radical polymerization and the obtained polymers are expected to be as functional polymers bearing the exo-methylene groups attached to the polymer backbone. We now wish to report the radical homopolymerization of phenylallene (PA) and the copolymerization of PA with vinyl monomers, since PA is considered to be a standard monomer in allene monomers in analogy with styrene in a variety of vinyl monomers, and no detailed study on the radical polymerization of PA has been reported.[3)] The functional polymer bearing the styryl structure on the polymer backbone will be obtained by homopolymerization or copolymerization of PA.


$CH_2{=}C{=}CH{-}OMe$

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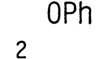
$CH_2{=}C{=}CH{-}OPh$

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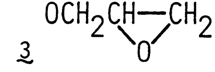
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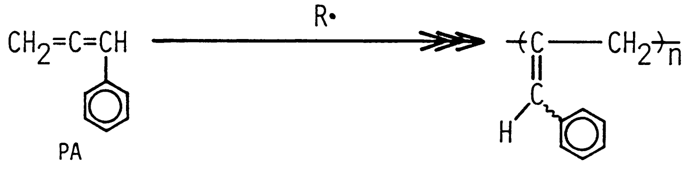


(1)

The requisite phenylallene was prepared by the reaction of methyl propargyl ether[4)] with phenylmagnesium bromide in the presence of copper (I) bromide according to the reported procedure.[5)] The radical polymerization of PA was carried out in the presence of azobis(isobutyronitrile) (AIBN), benzoyl peroxide (BPO), t-butylperoxy 3,5,5-trimethylhexanoate (TBP355), and di-t-butyl peroxide (DTBP) as radical initiators in bulk for 48 h at 60-120 °C. The soluble polymers were purified by dissolution in dichloromethane, followed by precipitation in methanol. The results are summarized in Table 1.

As shown in Table 1, PA polymerizes at 60-120 °C without crosslinking, and the polymer yield increases with higher polymerization temperature. The average molecular weight of the polymer is about 2000 irrespective of the temperature and is generally lower compared with that of polystyrene (vinyl analog of PA) obtained by the radical polymerization. The IR spectra of all polymers in Table 1 did not show an absorption at 890 cm^{-1} characteristic of an exo-methylene. The ^{1}H NMR spectra measured in $CDCl_3$ showed three broad singlets at δ 7.1 (aromatic protons), 6.3 (olefinic proton), and 2.4 ppm (methylene protons) of ratios 5:1:2. These spectral data indicate that the obtained polymers consist of one unit polymerized by the terminal double bond of PA (Eq. 1),[6)] and it is distinct from polymers of alkoxyallenes **1**-**3** which consist of two units polymerized by the respective 1,2- and 2,3-double bond of allenes.[1,2)]

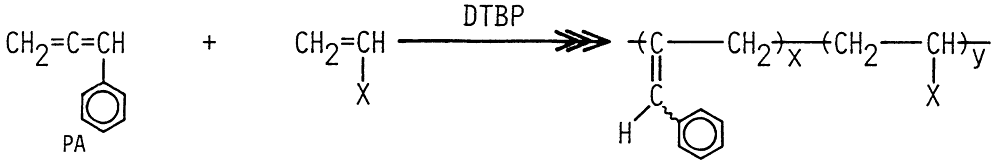
At the optimized conditions in the polymerization of PA, the copolymerization of PA with some vinyl monomers such as styrene (St), methyl methacrylate (MMA), methyl acrylate (MA), acrylonitrile (AN), and vinyl acetate (VAc) was carried out. Thus, an equimolar mixture of PA and the vinyl monomer was heated in the presence of DTBP (3 mol%) at 120 °C for 48 h. The soluble polymer was purified in a similar manner to the homopolymerization of PA except for the copolymerization of PA with AN.[7)] The results are summarized in Table 2.

Table 1. Radical homopolymerization of PA[a)]

Radical initiator	Temp / °C	Yield[b)] / %	$\bar{M}n$[c)]	$\bar{M}w/\bar{M}n$[c)]
AIBN	60	30	2000	2.04
BPO	80	31	2500	2.41
TBP355	100	48	2200	2.14
DTBP	120	46	2100	1.96

a) All polymerizations were carried out in bulk for 48 h in the presence of radical initiators (3 mol%). b) Insoluble polymer in methanol. c) Estimated by GPC (based on polystyrene).

Inspection of the results in the Table 2 reveals some characteristic features of the copolymerization of PA with the vinyl monomer. (1) Vinyl monomers such as St, MMA, MA, and AN can copolymerize with PA to afford the corresponding copolymers whose compositions are nearly 1:1. (2) The copolymer of PA with VAc contains only 5% of VAc, and accordingly VAc will not be a good comonomer for PA. (3) The average molecular weight of the copolymers are higher than that of the homopolymer of PA except the copolymer of PA with VAc. The IR spectra of all copolymers did not show an absorption at 890 cm^{-1} similarly to the homopolymer of PA; the ^1H NMR spectra also did not show the signal assignable to the exo-methylene protons at δ 5.0-5.3, which is observed in the polymer of alkoxyallenes **1**-**3**,[1,2] while the signals assignable to the aromatic protons at δ 7.2-7.1 ppm, the olefinic protons at δ 6.5-6.4 ppm, and the corresponding polymerized vinyl monomers were observed. These spectral data indicate that PA gives also one polymer unit polymerized by the terminal double bond of PA even in the copolymerization with various vinyl monomers (Eq. 2). By the radical copolymerization using PA, the unique units which are regarded as styrene attached to the polymer backbone can be easily introduced to commercially available polymers.



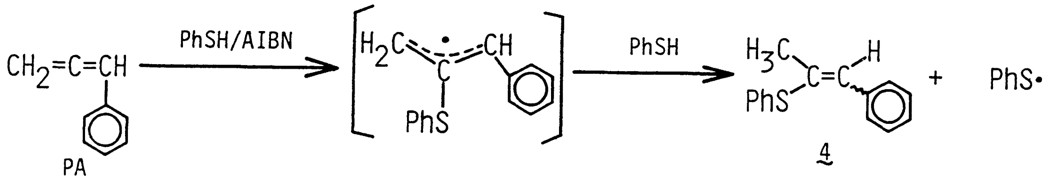
(2)

Table 2. Radical copolymerization of PA with vinyl monomers[a)]

Comonomer	Yield[b)] %	Composition / mol%[c)] x	Composition / mol%[c)] y	$\overline{M}n$[d)]	$\overline{M}w/\overline{M}n$[d)]
St	63	40	60	4700	2.48
MMA	32	52	48	2900	2.77
MA	18	60	40	3000	1.69
AN	13[e)]	44	56	2400	1.80
VAc	24	96	4	1900	1.94

a) An equimolar mixture of PA and the vinyl monomer copolymerized at 120 °C for 48 h in the presence of DTBP (3 mol%). b) Insoluble copolymer in methanol.
c) Determined by ^1H NMR. d) Estimated by GPC (based on polystyrene).
e) Insoluble copolymer in ether.

Furthermore, the radical reaction of PA with thiophenol was carried out as a model reaction of the polymerization. Thus, the mixture of PA and thiophenol was heated in the presence of AIBN at 60 °C for 48 h to give the product **4**[8] (Y. 65%) which is formed by addition of thiophenol to the terminal double bond of PA (Eq. 3).[9] The reaction process of PA and thiophenol corresponded entirely to the radical polymerization process of PA, and the propagating radical of the polymer is presumably assumed to attack the central carbon of allene in the polymerization, since a thiyl radical attacks the central carbon of allene to afford **4** in the model reaction.



(3)

In summary, the present work has demonstrated that the radical polymerization of PA affords the unique functional polymer to which the styryl structure attached, and that its unit can be easily introduced to various available polymers by the radical copolymerization of PA with vinyl monomers. These polymers are expected to undergo crosslinking or incorporation of other functional groups. Further works on the radical polymerization as well as ionic polymerizations of allene derivatives are in progress in our laboratory.

References

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6) This structure was also formed by the polymerization of PA with the use of N,N-tetrakis(trimethylsilyl)cobaltdiamine: J. Furukawa, J. Kuji, and K. Ueo, Makromol. Chem., 170, 247 (1973).

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8) Bp 106 °C/0.08 mmHg; IR (neat) 1610 cm^{-1}; ^1H NMR (CCl_4, TMS) δ 7.27 (s, 5H), 7.13 (s, 5H), 6.60 (s, 1H), 2.01 and 1.93 (2s, 3H).

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