Studies of the Polymerization of Diallyl Compounds. XXXVIII. Telomerization of Diallyl Aromatic Dicarboxylates in the Presence of Carbon Tetrabromide

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Synopsis

Radical telomerization of diallyl aromatic dicarboxylates, including diallyl phthalate (DAP) and diallyl terephthalate (DAT), was investigated in detail in the presence of CBr_4 as a telogen. Telomer yield could be accurately determined by a subsidiary GPC measurement in conjunction with a precipitation method. Telomerization kinetics of diallyl compound in the presence of CBr_4 was discussed and the chain transfer constant C_{CBr_4} $(= k_{tr}/k_p)$ was estimated to be 57.9 and 53.8 for DAP and DAT, respectively, the values which correspond to those for one functional group of diallyl compound. The degree of polymerization was significantly dependent on conversion as consequences of the fast consumption of CBr_4 and the occurrence of crosslinking reaction. The rate of polymerization was enhanced with the added amount of CBr_4, being ascribable to the replacement of the degradative chain transfer by the chain transfer to CBr_4, the latter which yields active tribromomethyl radical in lieu of less active allyl radical. Gelation was delayed with an increase in the added amount of CBr_4. Preparation of telomer in high yield and its applicability are finally discussed.

INTRODUCTION

As a consequence of our continuing interest in the radical polymerization of diallyl compounds,[1] the present article is concerned with the telomerization of diallyl dicarboxylates, mainly involving diallyl phthalate (DAP) as a typical, commercially important diallyl monomer, in the presence of carbon tetrabromide as a telogen. That is, our interest is basically centered on the addition effect of carbon tetrabromide on the kinetics of allyl polymerization involving degradative chain transfer and the gelation in the radical polymerization of diallyl compounds and, moreover, the possibility for application of the telomer obtained is discussed.

EXPERIMENTAL

Materials

DAP and DAT, commercially available reagents, were distilled *in vacuo* under nitrogen before use.

Benzoyl peroxide (BPO) and 2,2'-azobisisobutyronitrile (AIBN) as initiators were purified by conventional methods.

Carbon tetrabromide and carbon tetrachloride as telogens were commercially available special research grade reagents.

Telomerization Procedure

Telomerization was carried out in ampoules containing required amounts of monomer, initiator, and telogen at 80°C.

After a definite period of reaction time the telomer produced was precipitated by pouring the reaction mixture into a large amount of chilled petroleum ether for DAP polymerization or chilled n-hexane for DAT polymerization. In this treatment the telomer recovered contained a considerable amount of monomer which was determined by gel permeation chromatography (GPC). Measurements were carried out with a Waters Associates Model ALC/GPC 501 apparatus at room temperature under the following conditions: solvent, tetrahydrofuran (THF); polystyrene gel column combination, 60, 100, and 350 Å (Waters designation); sample concentration, 0.1% (w/v); and flow rate, 1 mL/min.

Gelation

The gelled reaction mixture was poured into chilled methanol to recover the polymer produced. The polymer was then subjected to a benzene extraction and the insoluble part was calculated as the content of gelled polymer.

Analyses

The number-average molecular weight of the telomer was determined by GPC. Measurements were carried out with a Waters Associates Model ALC/GPC 244 apparatus at room temperature under the following conditions: solvent, THF; μ styragel column combination, 10^2, 500, 10^3, 10^4, and 10^5 Å (Waters designation); polymer concentration, 0.1% (w/v); and flow rate, 1 mL/min. GPC curves were analyzed by using the calibration curve obtained with the fractionated poly-DAP, the molecular weight of which was measured by light scattering (LS). LS measurements were carried out in benzene at 30 ± 0.1°C in a Union Giken LS-601 automatic laser scattering photogoniometer over the angular range 30–150°, using unpolarized light of wavelength 632.8 nm. For the low molecular weight polymer the correction of the molecular weight was made by vapor pressure osmometry (VPO). VPO measurements were done by using a Hewlett-Packard 302 vapor pressure osmometer in benzene at 37°C.

The iodine value of the polymer was determined by the Wijs method. ^{1}H-NMR 100 MHz spectrum was obtained with a JEOL JNM-PS-100 instrument.

Photocrosslinking

DAP prepolymer containing required amount of telomer (II) was cast on glass plate from the 10 g/L dioxane solution, followed by evaporating the solvent under vacuum to obtain film, and then irradiated with UV light from a high-pressure mercury lamp made by Ushio Denki Co. (100 W) at a distance of 20 cm from the lamp at room temperature. The film was transparent and its thickness was around 2 μm. The irradiated film on glass plate was immersed in THF for 2 min and then, the insoluble part was successively reimmersed in fresh THF for 30 s, dried *in vacuo*, and weighed.

RESULTS AND DISCUSSION

Determination of Telomer Yield

For the purpose of isolating polymer from the reaction mixture consisting of unreacted monomer and polymer, precipitation methods are widely employed. In addition, vacuum evaporation of unreacted monomer from the reaction mixture is sometimes used when the boiling point of monomer is low.   However, both methods are not always adequate in this work because the molecular weight of the polymer produced is quite low, i.e., in the molecular weight range of telomer and the boiling point of monomer is too high to remove it by vacuum evaporation.

Thus, a subsidiary GPC measurement was carried out in conjunction with a precipitation method: First, the reaction mixture was poured into a large volume of petroleum ether to precipitate the polymer (I) containing a considerable amount of unreacted monomer, in this process which the complete recovery of the polymer produced was confirmed from the absence of the polymer in the petroleum ether extract which was vacuum-condensed and, then, the condensate was subjected to GPC measurement.   Second, the content of unreacted monomer in the polymer (I) was calculated from the GPC curve monitored by UV absorption at 254 nm; here it should be noted that the RI-monitored GPC curve is not always useful for this purpose because the refractive index of the telomer depends on the molecular weight, although it becomes constant for the polymer of a sufficient molecular weight.   As a typical example, Figure 1 shows the GPC curve of the polymer (I) obtained under the following polymerization conditions: $[CBr_4]/[DAP] = 1/10$, $[BPO] = 0.1$ mol/L, 80°C, 1 h, yield 20%.   The areas A and B correspond to monomer and polymer, respectively, and the ratio of both areas S_A/S_B was estimated using a planimeter; the calibration curve shown in Figure 2 was employed for the correction of the polymer (I) yield.

In this connection, the reprecipitation of the polymer (I) was unsuccessfully tried by employing a variety of solvent–nonsolvent systems; the complete removal of monomer from the polymer (I) was always accompanied by the loss of the low molecular weight polymer, i.e., dimer or trimer and so on.
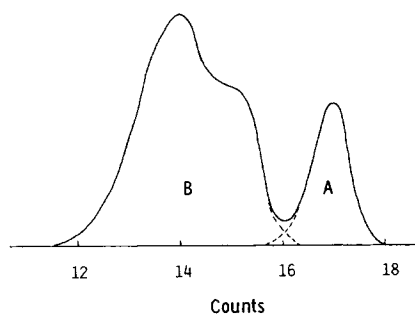

Counts

Fig. 1. GPC curve of the telomer (B) obtained as containing a considerable amount of unreacted monomer (A).
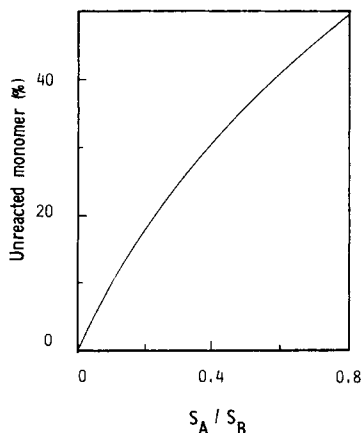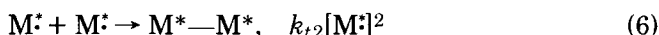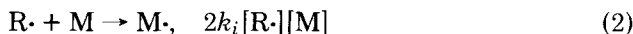
Fig. 2. Calibration curve for the determination of telomer yield from the GPC curve shown in Figure I.

Kinetics of Allyl Polymerization in the Presence of Telogen

We have discussed in detail the kinetics of allyl polymerization involving degradative chain transfer for diallyl compounds.[2,3]

Thus, when the reactivity of both uncyclized and cyclized radicals are assumed to be equivalent, the polymerization mechanism of diallyl compounds for the estimation of the rate and the degree of polymerization will be given as follows:

$$I \rightarrow 2R\cdot, \quad 2fk_d[I] \tag{1}$$

$$R\cdot + M \rightarrow M\cdot, \quad 2k_i[R\cdot][M] \tag{2}$$

$$M\cdot + M \rightarrow M\cdot, \quad 2k_p[M\cdot][M] \tag{3}$$

$$M\cdot + M \rightarrow P + M\overset{\cdot}{\cdot}, \quad 2k_{t1}[M\cdot][M] \tag{4}$$

$$M\overset{\cdot}{\cdot} + M \rightarrow M\cdot, \quad 2k_i'[M\overset{\cdot}{\cdot}][M] \tag{5}$$

$$M\overset{\cdot}{\cdot} + M\overset{\cdot}{\cdot} \rightarrow M^*—M^*, \quad k_{t2}[M\overset{\cdot}{\cdot}]^2 \tag{6}$$

where I is an initiator, M, a diallyl monomer; P, the polymer produced; R·, the initiator radical; M·, the uncyclized or cyclized growing polymer radical; and M$\overset{\cdot}{\cdot}$, the allyl radical.

If a steady state is assumed for the different types of radicals, eqs. (7)–(9) can be obtained:

$$[R\cdot] = fk_d[I]/k_i[M] \tag{7}$$

$$[M\cdot] = \frac{1}{k_{t1}[M]}\left\{fk_d[I] + k_i'\left(\frac{2fk_d[I]}{k_{t2}}\right)^{1/2}[M]\right\} \tag{8}$$

$$[M\overset{\cdot}{\cdot}] = (2fk_d[I]/k_{t2})^{1/2} \tag{9}$$

Here f denotes the efficiency of the initiation of the polymer radical by R·.

The rate and the degree of polymerization were then derived as eqs. (10) and (11); here it should be noted that the dimer, M*—M*, produced by coupling of allyl radicals, i.e., eq. (6), was present in the polymer recovered, as is evident from
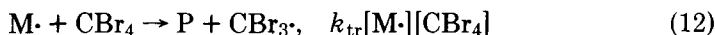
the experimental procedure mentioned above:

$$R_p = 2k_i[\text{R}\cdot][\text{M}] + 2(k_p + k_{t1})[\text{M}\cdot][\text{M}] + 2k_i'[\text{M}^*][\text{M}]$$

$$= \left(2 + \frac{k_p}{k_{t1}}\right)\left\{2fk_d[\text{I}] + 2k_i'\left(\frac{2fk_d[\text{I}]}{k_{t2}}\right)^{1/2}[\text{M}]\right\} \quad (10)$$

$$\overline{P}_n = R_p/(2k_{t1}[\text{M}\cdot][\text{M}] + k_{t2}[\text{M}^*]^2)$$

$$= \left(2 + \frac{k_p}{k_{t1}}\right)\left\{\frac{fk_d[\text{I}] + k_i'(2fk_d[\text{I}]/k_{t2})^{1/2}[\text{M}]}{2fk_d[\text{I}] + k_i'(2fk_d[\text{I}]/k_{t2})^{1/2}[\text{M}]}\right\} \quad (11)$$

Here it should be noted that eqs. (10) and (11) are applicable only to the polymer obtained in the early stage of polymerization, in which the crosslinking reaction is negligible.

Now, we have to consider the addition effect of carbon tetrabromide as a telogen, i.e., a strong chain transfer reagent, the addition of only a small amount of which reduces drastically the degree of polymerization, although the rate of polymerization is scarcely affected; for the polymerization of diallyl compound in the presence of a small amount of carbon tetrabromide the following two elementary reactions, eqs. (12) and (13), will be simply given in addition to eqs. (1)–(6):

$$\text{M}\cdot + \text{CBr}_4 \rightarrow \text{P} + \text{CBr}_3\cdot, \quad k_{\text{tr}}[\text{M}\cdot][\text{CBr}_4] \quad (12)$$

$$\text{CBr}_3\cdot + \text{M} \rightarrow \text{M}\cdot, \quad 2k_i''[\text{CBr}_3\cdot][\text{M}] \quad (13)$$

Here it should be noted that the ability of tribromomethyl radical to reinitiate a new polymer chain is sufficiently large compared with allyl radical, i.e., $k_i'' \gg k_i'$ and, thus, the influence of the addition of a small amount of carbon tetra-

bromide on the rate of polymerization is small compared with the degree of polymerization; this was tentatively checked for the polymerization of DAP and DAT, although the addition of a considerable amount of carbon tetrabromide gave an appreciable influence on the rate of polymerization as will be discussed later in detail.

Thus, the degree of polymerization is given as follows:

$$\overline{P}_{n,\text{tr}} = \frac{R_p}{2k_{t1}[\text{M}\cdot][\text{M}] + k_{t2}[\text{M}^*]^2 + k_{\text{tr}}[\text{M}\cdot][\text{CBr}_4]} \quad (14)$$

Then,

$$\frac{1}{\overline{P}_{n,\text{tr}}} = \frac{1}{\overline{P}_n} + \frac{k_{tr}[\text{M}\cdot][\text{CBr}_4]}{R_p} = \frac{1}{\overline{P}_n} + \left(\frac{k_{tr}}{4k_{t1} + 2k_p}\right)\frac{[\text{CBr}_4]}{[\text{M}]}$$

$$= \frac{1}{\overline{P}_n} + \left(\frac{1}{4k_{t1}/k_p + 2}\right)C_{\text{CBr}_4}\frac{[\text{CBr}_4]}{[\text{M}]} \quad (15)$$

where $C_{\text{CBr}_4} (= k_{\text{tr}}/k_p)$ corresponds to the chain transfer constant for one functional group of diallyl compound.

Determination of Chain Transfer Constant

Now, we tried to estimate the chain transfer constant C_{CBr_4} in the polymerization of DAP and DAT. Noteworthily, the dependence of the degree of polymerization on conversion for the polymerization in the presence of a strong chain transfer reagent should be quite large, and, moreover, for the polymer-
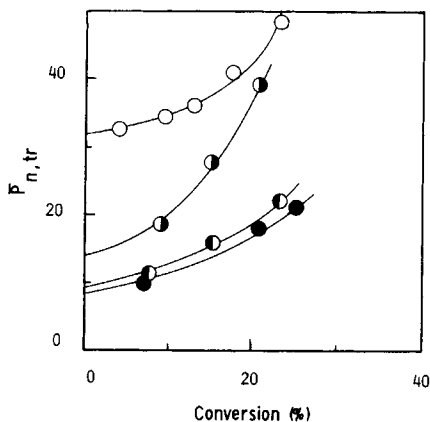
Fig. 3. Dependence of $\overline{P}_{n,tr}$ on conversion in the polymerization of DAP using CBr$_4$ as a telogen: [CBr$_4$]/[DAP] = 0 (○); 1/1000 (◐); 1/500 (◑); 1/300 (●).

ization of diallyl compounds such as DAP and DAT the crosslinking reaction becomes important with the progress of polymerization; the conversion dependency of the degree of polymerization was carefully checked. Figures 3 and 4 show the bulk polymerization results of DAP and DAT, respectively, at 80°C in the presence of carbon tetrabromide; in both polymerizations the conversion dependency of the degree of polymerization was quite large, as expected. The reciprocal of the initial degree of polymerization obtained by the extrapolation to zero conversion from the experimental results shown in Figures 3 and 4 are plotted in Figure 5 against the molar ratio of carbon tetrabromide to monomer, [CBr$_4$]/[M], in order to estimate the chain transfer constant employing eq. (15); good linear relationships were obtained and, thus, the values of C_{CBr_4} were estimated to be 57.9 and 53.8 for DAP and DAT, respectively, in which the value of k_{t1}/k_p is assumed to be 0.03.[4,5] These values are quite high in comparison with those for common vinyl monomers[6]; that is, even in the case of vinyl acetate as a typical unconjugated monomer, the C_{CBr_4} value is reported as 2.87 at 70°C.[7] This is ascribable to the high unconjugation of carbon-carbon double
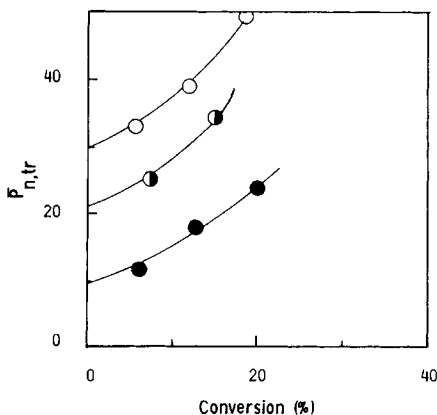

Fig. 4. Dependence of $\overline{P}_{n,tr}$ on conversion in the polymerization of DAT using CBr$_4$ as a telogen: [CBr$_4$]/[DAT] = 0 (○); 1/2100 (◐); 1/380 (●).
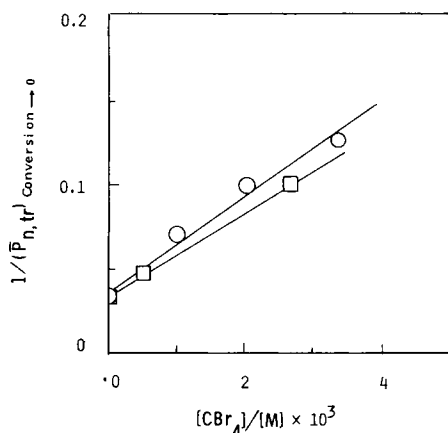
Fig. 5. Graphs for the determination of the chain transfer constant employing eq. (15) in the polymerization of DAP (O) and DAT (□) using CBr_4 as a telogen.

bond in allyl monomers.[1,8] In this connection, the chain transfer constant C_{CCl_4} for the polymerization of DAP in the presence of carbon tetrachloride was tentatively estimated to be 1.82, whereas for the polymerization of vinyl acetate the value of C_{CCl_4} is obtained as 0.20 at 70°C.[7]

Moreover, the value of C_{CBr_4} in the polymerization of DAP was somewhat higher than that in the DAT polymerization; this may be attributed to lowering of the reactivity of the cyclized radical in the polymerization of DAP.[1,4,9]

Addition Effect of Carbon Tetrabromide on Rate of Polymerization

The influence of the addition of carbon tetrabromide on the rate of polymerization was examined in detail in the presence of a considerable amount of carbon tetrabromide; Figure 6 shows the time-conversion curves for the polymerization of DAP at 80°C, using 0.1 mol/L of BPO as the initiator. The initial rate of polymerization was quite enhanced by the addition of carbon tetrabromide; this
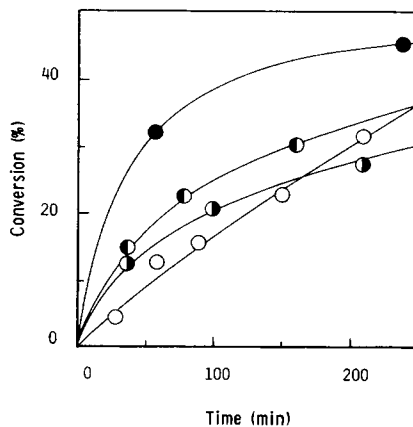

Fig. 6. Time-conversion curves for the polymerization of DAP using CBr_4 as a telogen with 0.1 mol/L of BPO at 80°C: $[CBr_4]/[DAP] = 0$ (O); 1/15 (◑); 1/10 (◒); 1/5 (●).
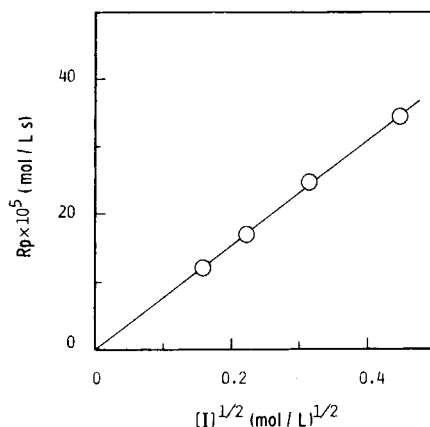
Fig. 7. Square root dependency of R_p on [I] in the polymerization of DAP using CBr$_4$ as a telogen with BPO as an initiator.

was also reconfirmed by using AIBN as the initiator since the rate of decomposition of BPO might be accelerated by the addition of carbon tetrabromide. Thus, this kind of rate feature is attributable to the diminution of a degradative chain transfer, i.e., eq. (4), with the addition of carbon tetrabromide: In the polymerization of allyl compounds the hydrogen atoms attached to the carbon atom alpha to the carbon–carbon double bond are responsible for degradative chain transfer, and the resulting allyl radical M$\cdot$ is less active and/or has less tendency to initiate a new polymer chain because of an ability to stabilize itself by resonance. Therefore, the chain transfer is essentially a termination reaction. However, in the telomerization using carbon tetrabromide as a telogen the chain transfer reaction of the growing polymer radical to carbon tetrabromide, i.e., eq. (12), is comparable or preferential to eq. (4) and yields active tribromomethyl radical in lieu of less active allyl radical. For example, as is evident from the comparison of $k_{t1}/k_p \simeq 0.03$ with $k_{tr}/k_p \simeq 60$ for the polymerization of DAP, the chain transfer constant k_{tr} of the growing polymer radical to carbon tetrabromide is about 2,000 times larger than that k_{t1} to DAP monomer. Thus, in the polymerization of DAP at [CBr$_4$]/[DAP] = 1/10, the degradative chain transfer should be replaced by the chain transfer to carbon tetrabromide, resulting in the square root dependency of the rate of polymerization on the initiator concentration as shown in Figure 7, although in the polymerization of diallyl compounds the rate of polymerization is not proportional to the square root or the first power of the initiator concentration,[1,2,3,10,11] as is evident from eq. (10).

Gelation in the Presence of Telogen

In the preceding section, the polymerization mechanism at an early stage of polymerization in the presence of telogen, in which the crosslinking reaction is negligible, was discussed in detail. However, the crosslinking reaction between the pendant double bond of the telomer produced and the growing chain radical gradually becomes important as the polymerization proceeds and, eventually, gelation occurs, although the gel-point conversion is surely delayed compared
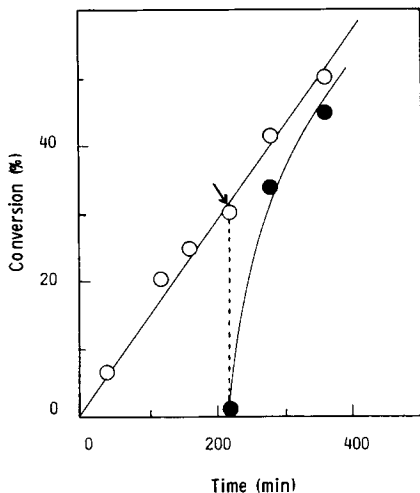
Fig. 8. Graph for the determination of gel-point conversion in the polymerization of DAP using CBr$_4$ as a telogen at [CBr$_4$]/[DAP] = 1/300 with 0.1 mol/L of BPO: (O) total polymer; (●) gel polymer; (↓) gel point.

with the polymerization in the absence of telogen as a consequence of the reduction of the polymer chain length.

Figure 8 shows the graph for the determination of the gel-point conversion in the polymerization of DAP in the presence of carbon tetrabromide at [CBr$_4$]/[DAP] = 1/300 as an example; thus, the gel point was estimated as the conversion at the time, at which gel starts to form.   In Figure 9 are given the relationships between the gel-point conversion or the extrapolated primary chain length to zero conversion, $\overline{P}_{n,0}$, and [CBr$_4$]/[DAP]; gelation was delayed with an increase in the added amount of carbon tetrabromide.   However, the delay was not so remarkable as compared with a drastical reduction of $\overline{P}_{n,0}$; this is due to the fast consumption of carbon tetrabromide compared to DAP monomer, resulting in the decrease of the molar ratio of carbon tetrabromide to the unreacted
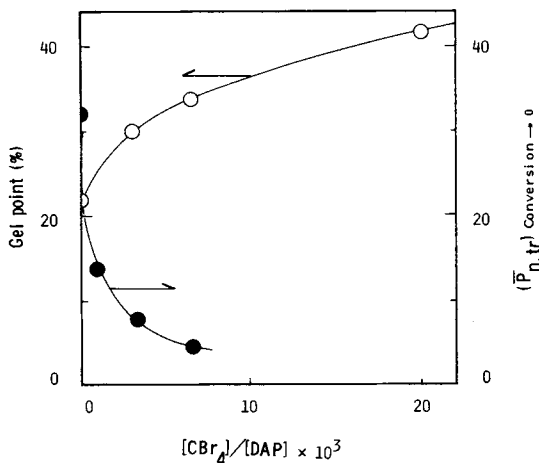

Fig. 9. Relationships between the gel-point conversion or the primary chain length and [CBr$_4$]/[DAP] in the polymerization of DAP using CBr$_4$ as a telogen.
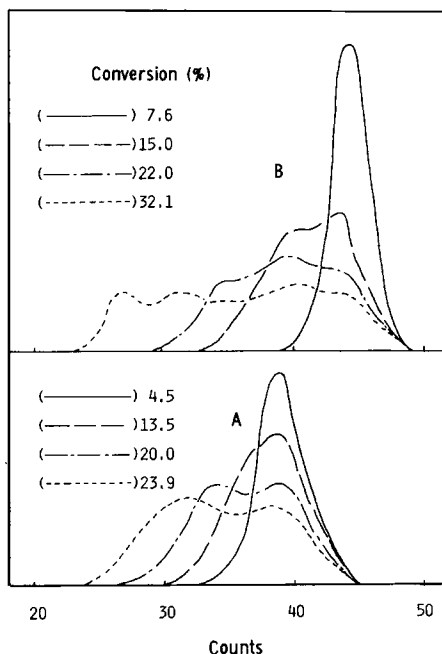
Fig. 10. Comparison of the conversion dependency of GPC curves of the polymer obtained at $[CBr_4]/[DAP] = 0$ (A) and 1/50 (B). Conversion (%): (B) (—) 7.6; (– – –) 15.0; (– · –) 22.0; (- - - -) 32.1; (A) (—) 4.5; (– – –) 13.5; (– · –) 20.0; (- - - -) 23.9.

DAP monomer in the polymerization system with conversion and, thus, the increase of the primary chain length of the polymer produced at a higher conversion. This point was clearly illustrated in Figure 10 as a comparison of the conversion dependency of GPC curves of the polymers obtained in the polymerization at $[CBr_4]/[DAP] = 1/50$ with that of the polymers obtained in the polymerization of DAP in the absence of carbon tetrabromide.

Preparation of Telomer in High Yield and Its Applicability

It is well known that there has been commercial interest in allyl resins represented by DAP resin because of their excellent electrical properties and ability to maintain these under conditions of high temperature and humidity, their excellent dimensional stability, and chemical resistance.[12,13] Thus DAP telomer should find versatile use when the telomer is prepared in high yield.

In this connection, we examined in detail the polymerization conditions for the obtainment of the telomer in high yields, i.e., how to delay the gelation up to higher conversion. Here it should be recalled that the chain transfer constant is dependent on the chain length n of the growing polymer radical, $YM_n\cdot$, in which telogen is expressed as XY; for example, in the telomerization of ethylene in the presence of carbon tetrachloride the C_n values were obtained to be 0.10, 3.0, 7.0, 10.3, 13.3, and 13 for $n = 1, 2, 3, 4, 5$, and ∞, respectively, being due to polar interactions.[14] This suggests the possibility of obtaining the telomer in high yield for the polymerization of DAP in the presence of a large amount of carbon tetrabromide. Thus the telomer (II) was obtained in 75% yield in the polymer-
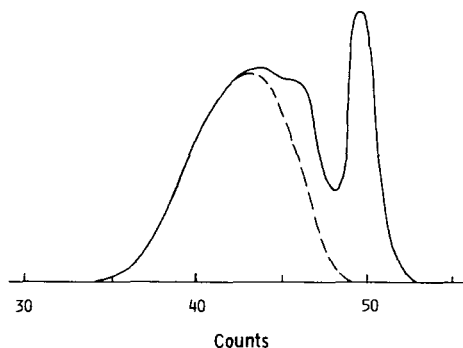
Fig. 11. GPC curves of the telomer obtained in 75% yield in the polymerization at [CBr$_4$]/[DAP] = 1/3: (—) before and (- - - - -) after reprecipitation.

ization at [CBr$_4$]/[DAP] = 1/3 and at 80°C, using 0.3 mol/L of BPO as the initiator. In Figure 11 is given the GPC curve of the telomer (II), demonstrating a rather narrow molecular weight distribution. The telomer (II) was carefully reprecipitated from benzene–petroleum ether system, although the GPC curve of the telomer recovered at 55% after reprecipitation is shown in Figure 11 as a dotted line and, then, subjected to chemical and spectral analyses: molecular weight, 2350 by VPO; iodine value, 35.8; C, 45.52%; Br, 33.53%. Also, Figure 12 shows the NMR spectrum of the telomer, indicating the presence of a considerable amount of unreacted pendant allyl groups in the conformity of the iodine value, although the structure of the telomer is discussed later in detail.

This kind of telomer may have the wide applicability to commercial use: for example, the telomer containing bromine atoms is used in flame-resistant compositions. In addition, the telomer having tribromomethyl group is self-photocrosslinkable or useful as photosensitizer; Figure 13 shows the photosensitivity of DAP prepolymers in the absence or presence of the telomer (II), the photocrosslinking reaction of DAP prepolymer being enhanced by the addition of the telomer (II). Moreover, the high responsibility of tribromomethyl group for chain transfer reaction may demonstrate the applicability to the preparation of block cotelomers since the copolymerizability of allyl compound with common conjugated vinyl monomers is quite low,[1] although the details are now in progress.
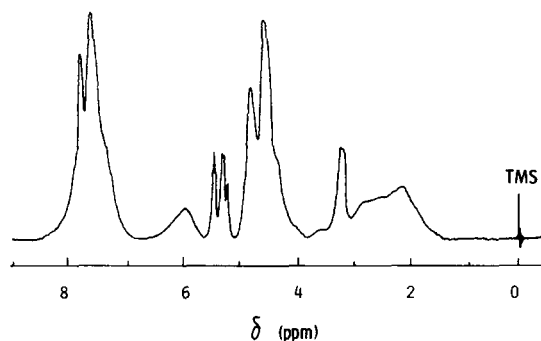

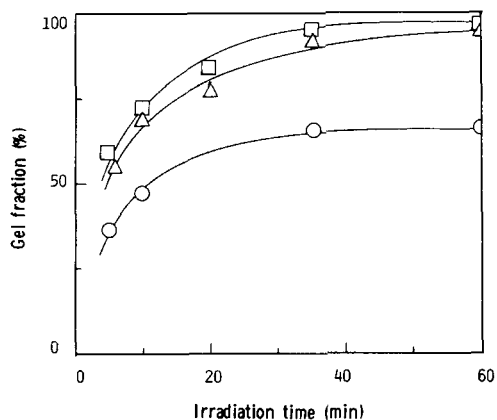Fig. 12. ^{1}H-NMR spectrum of the telomer (II) (100 MHz, in CDCl$_3$, at 23°C).

Fig. 13. Photosensitivity of DAP prepolymers in the presence of the telomer (II) of (O) 0%; (△) 12%; and (□) 35%.

Structure of Telomers

Finally, we will discuss briefly the structure of the resulting telomers from the following two standpoints: first, for the telomers obtained at an early stage of polymerization the crosslinked structure can be negligible. Thus the structure of both DAP and DAT telomers, obtained under the polymerization conditions where the degradative chain transfer is replaced by the chain transfer to carbon tetrabromide, are depicted as follows:

DAP telomer

DAT telomer
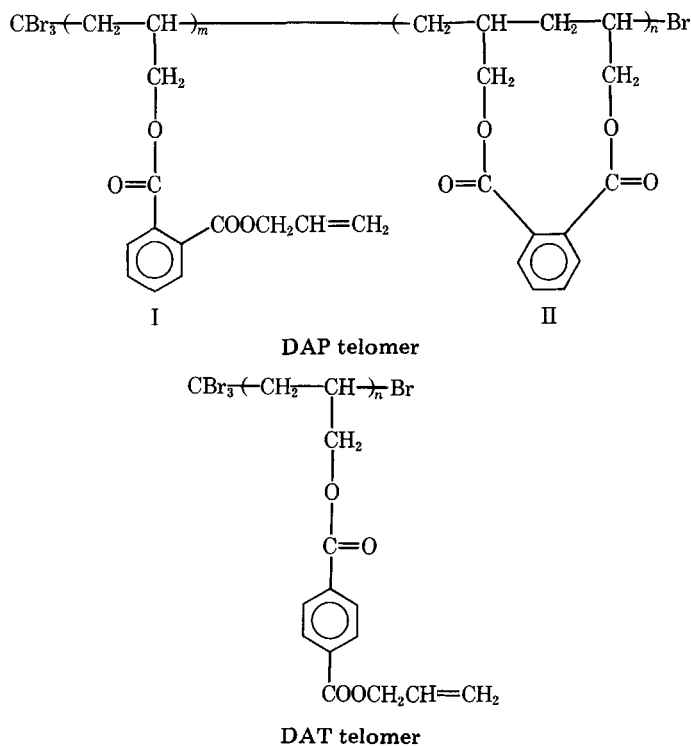
Here the value of m/n for DAP telomer is expected to be 1.33 from the bulk polymerization result,[2] and, moreover, the cyclic structure II is predominantly an 11-membered ring formed via consecutive intramolecular head-to-tail addition of the uncyclized radical.[15] For DAT telomer a large cyclic structure formation leading to around 10% loss of unreacted pendant allyl groups[16] might occur via nonconsecutive intramolecular addition, in which uncyclized radical adds to any other double bond pendant to the chain than to the double bond present in the same monomer unit, although the intramolecular cyclization in the monomeric DAT unit is impossible in view of the molecular model.

Second, for the telomer and/or polymer obtained at a higher conversion when the crosslinking is significant, the structure is complexed depending on the polymerization conditions because the rate of consumption of carbon tetrabromide is fast compared to DAP monomer, leading to the increase of the primary chain length of the telomer produced at a higher conversion, and the crosslinking between the pendant double bond of the telomer and the growing chain radical gradually becomes important with the progress of polymerization, both of which affect the molecular weight distribution of the telomer and/or polymer obtained.

In this connection, the telomer (II) was obtained in 75% yield in the polymerization at $[CBr_4]/[DAP] = 1/3$ as mentioned above; from the analytical results of carbon and bromine contents and molecular weight the structure of the telomer assumed as $(CBr_3)_m(DAP)_nBr_m$ was determined to be $m = 2.48$ and $n = 6.20$, the analytical results being recalculated in a good agreement with the experimental results: molecular weight, 2349; C, 45.65%; Br, 33.74%. Moreover, the number of unreacted pendant allyl groups, i.e., the uncyclized structural units I, was estimated at 3.31 from the iodine value; then, the cyclized units II are calculated to be 1.41 because the number of crosslinked units corresponds to m − 1, i.e., 1.48. These results suggest that the intramolecular cyclization of uncyclized radical in the polymerization of DAP is suppressed in the telomerization, as is evident from the comparison with the bulk polymerization result[2] described above. That is, the extent of cyclization of the telomer may depend on the chain length, i.e., the cyclization be enhanced with increased degree of polymerization. This suggestion is considered quite important for the comprehensive understanding of the cyclopolymerization behavior of nonconjugated dienes; thus the details will be discussed in our subsequent article.[17]

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