Chain Transfer to Telomer[1]*. II. In the Case of Catalyzed β-Polymerization*

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In the previous report[1] the transfer constants of telomer prepared by the thermal polymerization of styrene in a carbon tetrachloride solution were determined in the thermal β-polymerization[2] of styrene as $C_{\mathrm{M}}=2\times10^{-4}$ and $KC_{\mathrm{E}}=4\times10^{-2}$ (at 100°C) by the method previously suggested by Schulz et al.[3], where C_{M} and KC_{E} are the chain transfer constants belonging respectively to the middle part and to the end along the telomer chain. However, at a high rate of conversion of monomer, C_{M} and KC_{E} values were lower than the above values. In other words, a somewhat greater degree of polymerization was obtained than that at the lower conversion rate. The present investigation is concerned with this problem.

Moveover, the present report treats the effect of the presence of a catalyst on the apparent degree of polymerization. The contribution of a catalyst in β-polymerization has not been discussed by any other investigators but Hayes[4], who observed the graft efficiency in the emulsion polymerization. Such an observation appears to be a more logical consequence of the chain transfer reaction of a catalyst radical with the α-polymer competing with the usual initiation reaction. Although his findings can not be applied directly to the present homogeneous polymerization, in order to examine the effect of such a catalyst chain transfer reaction experimentally, the following experiments were carried out by polymerizing styrene in the presence of azobisisobutyronitrile (AIBN) as a catalyst and telomer as a α-polymer. The experimental conditions differed from those of the previous report only in the addition of 1 ml. of the catalyst solution to the mixture of styrene (5 ml.) and α-polymer in β-polymerization.

Experimental

Materials.—Styrene was purified by washing it with alkali and water to remove the inhibitor, drying it with calcium chloride, and distilling it twice under reduced pressure. G. R. grade benzene and carbon tetrachloride were distilled before use.

α-Polymer was prepared by uncatalyzed styrene-carbon tetrachloride polymerization at 100°C. Ampoules were thoroughly cleaned with chromic acid, washed with water and then with steam, and dried. α-Polymer was precipitated with methyl alcohol and dried.

The degree of polymerization of β-polymer, P_β, was determined from the relation of $P_{\mathrm{n}}=K[\eta]^a$, (where P_{n} indicates the degree of polymerization, $[\eta]$, the intrinsic viscosity, and K and a are constants)[5]. The viscosity measurements were done in a benzene solution at 30°C. The fractionation of α-polymer (telomer) was not carried out for the reason stated previously[1].

Procedures.—The catalyst solution consists of AIBN 0.1623 g. in benzene 100 ml. Mixtures of 5 ml. of styrene, various amounts of telomer, and 1 ml. of the catalyst solution were taken in the ampoules, frozen in dry ice, evacuated and sealed. The polymerizing temperature is 100°C, and its time, 1 hr. and 20 min. As the concentrations of the catalyst were in the range of from 1.56 to 1.67×10^{-3} mol./l. in all the experiments, the largest difference in the overall rates between minimum and maximum concentrations of the catalyst is still with in the range of experimental error. Total polymers were precipitated with methyl alcohol and dried.

The total polymer obtained by the above procedures was weighed. (This gives $W+W_\alpha$ according to a definition proposed below.)

The intrinsic viscosities for the total polymer were measured in a benzene solution at 30°C by the use of an Ostwald viscometer.

Results

The experimental results are summarized in Table I, in which the intrinsic viscosity of β-polymer, $[\eta]_\beta$, freshly produced in the presence of α-polymer, was calculated from the relation between the intrinsic viscosities of α-polymer, $[\eta]_\alpha$, and that of the total polymer, $[\bar{\eta}]$, which is expressed by the equation

$$[\bar{\eta}]=W_\alpha[\eta]_\alpha+W_\beta[\eta]_\beta \qquad (1)$$

where, W_α and W_β are the weight fractions of α- and β-polymers respectively. At this

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[1] Part I of this series, S. Okamura and K. Katagiri, *Makromol. Chem.*, **28**, 177 (1958).

[2] β-Polymerization indicates that in the presence of telomer (α-polymer).

[3] G. Henrici-Olivé, S. Olivé and G. V. Schulz, *Makromol. Chem.*, **23**, 207 (1957).

[4] R. A. Hayes, *J. Polymer Sci.*, **11**, 531 (1953).

[5] F. R. Mayo et al., *J. Am. Chem. Soc.*, **73**, 1691 (Eq. VI) (1951).

time the weight fraction of monomer converted, W, is conveniently assumed to be equal to W_β. The values of $[\eta]_\beta$ calculated above will be discussed later on the basis of a consideration of a less abbreviated equation than Eq. 1,

A plot of $1/P_\beta$ against the ratio of the concentration of α-polymer to that of monomer [Poly]/[M] is presented in Fig. 1 with the aid of the data shown in Table I. In the present report, P_β was not corrected for the small change in the rate of polymerization, because of that changes small effect on P_β.

In the previous report the acceleration of the rate at the high concentration and at the high degree of α-polymer was explained by the gelation effect, but this is not true in the present case because of the addition of benzene to the polymerizing system.

Discussion

By comparing our present findings with the previous results, the conversion of monomer in the present experiment is found to be present to the extent given in the previous report. In both cases, W is comparable with W_α. Although in the present reports P_β is lowered by the addition of catalyst, the limiting condition of $[\eta]_\alpha \ll [\eta]_\beta$ holds. As the gelation effect is not observed at present, the very confused features revealed in Fig. 1 seem to come from the presence of a catalyst. Therefore, it seems that the catalyst plays an important role through the reaction discussed below.

An inactive compound X and a telomer radical T·, which afterward becomes a block polymer, are produced as a consequence of the polymer transfer reaction of the radical R· produced from AIBN or a polymer radical $M_n\cdot$ with a telomer T shown below, with the reaction containing β-polymer:

$$\mathrm{R\cdot\ (and\ M_n\cdot) + T \rightarrow X + T\cdot}$$

$$\mathrm{R\cdot\ (and\ M_n\cdot) + \beta\text{-Polymer}}$$
$$\mathrm{\rightarrow X + \beta\text{-Polymer\ radical}}$$
$$\text{(Catalyzed } \beta\text{-polymer)}$$

The amount of block polymer increases more in the catalyzed β-polymerization than in the thermal polymerization, where the polymer transfer reaction occurs only by:

$$\mathrm{M_n\cdot + T \rightarrow M_n + T\cdot}$$

$$\mathrm{M_n\cdot + \beta\text{-Polymer} \rightarrow X + \beta\text{-Polymer\ radical}}$$
$$\text{(Thermal } \beta\text{-polymer)}$$

where M_n is the dead polymer containing n monomer units. The above discussion is also supported by the finding of Henrici-Olivé and Olivé[6] that the ratio of rate constants $(k_{\mathrm{tri}}/k_{\mathrm{st}})$ of the following reactions is about 10^{-1}:

$$\mathrm{R\cdot + M} \rightarrow k_{\mathrm{st}}$$

$$\mathrm{R\cdot + Polystyrene} \rightarrow k_{\mathrm{tri}}$$

The above reactions containing catalyst radicals are considered to make W_{B} and $W_{\beta\beta}$ larger than in the absence of a catalyst, where W_{B} and $W_{\beta\beta}$ are the weight fractions of the block polymer and the branched β-polymer which is produced from the reaction of β-polymer with the growing or catalyst radicals respectively. Thus, with the same extent of conversion, W_{B} and $W_{\beta\beta}$ are comparatively larger than those obtained in the previous report.

Accordingly, Eq. 1 used in the calcution of P_β in Table I becomes inadequate when applied to the present case, in which a large amount of block and branched polymer are produced. One must return to the unabbreviated form[1], i. e., to Eq. 2.

If Z is defined by $2[\eta]_\alpha[\eta]_\beta/([\eta]_\alpha+[\eta]_\beta)$ and $[\eta]_{\beta\beta}$ is the intrinsic viscosity of the branched β-polymer, one obtains:

$$[\bar{\eta}] = W_\alpha[\eta]_\alpha + (W - W_{\beta\beta})[\eta]_\beta + W_{\mathrm{B}}Z + W_{\beta\beta}[\eta]_{\beta\beta} \qquad (2)$$

And if $[\eta]_{\beta\beta}$ is assumed to be approximately equal to $2[\eta]_\beta$, Eq. 3 can be derived:

$$[\bar{\eta}] = W_\alpha[\eta]_\alpha + W[\eta]_\beta + W_{\mathrm{B}}Z + W_{\beta\beta}[\eta]_\beta \quad (3)$$

It can be seen that the $[\eta]_\beta$ value in Eq. 3 increases if $W_\beta Z + W_{\beta\beta}[\eta]_\beta$ is neglected. By the use of C_{M} and KC_{E} values obtained in the previous report, the actual $[\eta]_\beta$ value, which is, for the sake of convenience, defined as $[\eta]_\beta'$ in Table II, is calculated when it is

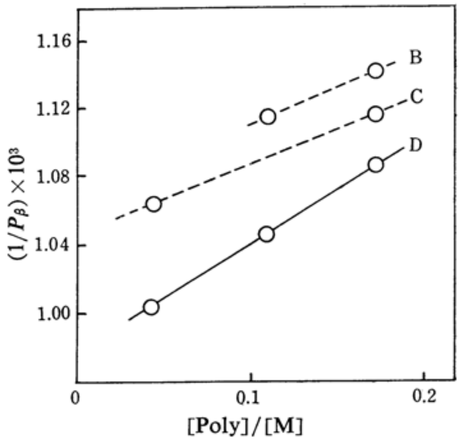

Fig. 1. Plots of $1/P_\beta$ against [Poly]/[M] indexes are to be referred to Table I.

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[6] G. Henrici-Olivé and S. Olivé, *Makromol. Chem.*, **27**, 166 (1958).

TABLE I. THE DEGREE OF POLYMERIZATION OF β-POLYMER CALCULATED BY EQ. 1.

	α-Polymer g.	β-Polymer g.	$[\bar{\eta}]$ 100 cc./g.	$[\eta]_\beta$ 100 cc./g.	$(1/P_\beta)\times 10^5$	[Poly]*/[M]
B1	0.500	0.756	0.466	0.656	111.3	0.110
B2	0.800	0.751	0.408	0.645	114.1	0.176
C1	0.200	0.699	0.562	0.680	106.3	0.044
C2	0.800	0.765	0.399	0.657	111.5	0.176
D1	0.200	0.704	0.555	0.708	100.2	0.044
D2	0.500	0.778	0.426	0.689	104.3	0.110
D3	0.800	0.766	0·339	0.669	108.5	0.176
Without α-polymer	0	0.703	—	0.650	113.0	0

$[\eta]_\alpha$, Values of α-polymers are as follows.

	B	C	D
$[\eta]_\alpha$	0.180	0.151	0.016

* [Poly] indicates the concentration in monomer unit mol./l.

TABLE II. VALUES OF $[\eta]_\beta{}'$ AND $W_BZ+W_{\beta\beta}[\eta]_\beta{}'$

	P_α	$[\eta]_\beta{}'$	$W_BZ+W_{\beta\beta}[\sigma]_\beta{}'$
B1	136	0.652	0.002
B2		0.636	0.004
C1	69	0.672	0.006
C2		0.628	0.014
D1	29	0.690	0.014
D2		0.643	0.028
D3		0.602	0.037

P_α, the degree of α-polymer is calculated by the following equation⁷⁾,

$$P_\alpha=(2-x)[M]_0/2C_S[S]_0$$

where $[M]_0$: the initial concentration of monomer
$[S]_0$: the initial concentration of solvent
C_S : the chain transfer constant of solvent
x : the conversion ratio of monomer to polymer

assumed that the intercept of each line at [Poly]/[M] = 0 in Fig. 1 remains constant. The $W_BZ+W_{\beta\beta}[\eta]_\beta$ value may also be calculated as shown in Table II, which shows that the value increases with the increase in [Poly]/[M] and as it moves from the B to the D group; the somewhat greater degree of polymerization at a high rate of conversion in the previous paper can be explained from the same discussion even for uncatalyzed β-polymerization.

Although $W_{\beta\beta}$ and W_B are not obtainable separately by the present treatment, the kinetical attempt of using the considerable elementary reactions was suggested in the styrene-carbon tetrachloride polymerization⁷⁾.

It may be concluded that $W_{\beta\beta}$ and W_B are increased by the reactions between a catalyst radical and a telomer or a β-polymer under the same experimental conditions as those of the previous report except for the presence of a catalyst. Therefore, the apparent degrees of polymerization of β-polymer larger than they actually are.

Summary

Catalyzed styrene polymerization in the presence of azobisisobutyronitrile and telomer has been carried out to investigate the effects of the conversion of monomer and of the addition of catalyst on the degree of polymerization of polymer under the same conditions as in the previous report.

The apparent degree of polymerization of polymer was obtained as a rather larger value than expected. This situation is qualitatively explained by the reactions of a catalyst fragment radical with telomer and with polymer freshly produced.

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7) S. Okamura and K. Katagiri, *Chem. High Polymers Japan (Kobunshi Kagaku)*, **16**, 173 (1959).