actually observed relation between these two quantities is described closely by Domb–Barrett's semiempirical equation proposed very recently. This fact affords a method for evaluating the binary cluster integral β for a given polymer–solvent system from measurement of α_s.

(2) As the polymer coil undergoes increased expansion by volume exclusion, Ψ becomes constant (0.22 ± 0.01) for $\alpha_s^3 > 7$. Before reaching this asymptotic limit Ψ decreases slightly with increasing α_s, in disagreement with the predictions of any two-parameter theories available at present for A_2.

(3) Log–log plots of α_η^3 vs. α_s^3 are approximately fitted by a straight line with a slope of 0.90 ± 0.02, except in the region of α_s near unity. This result indicates that the Flory viscosity factor Φ decreases steadily as the polymer coil is expanded more by volume exclusion.

The maximum value of α_s (about 2.4) attained in the present work is the largest of those reported so far, as far as we know. Our experimental results indicate that the behavior of a polymer coil in dilute solution already enters into the asymptotic region when it is expanded by excluded volume effect above α_s as large as 2. It is hoped that further studies are attempted to check this conclusion with data on other polymer–solvent systems.

Finally, we must refer to an important point which has not been given a serious consideration in the above presentation. It is the polydispersity of the polymer fractions used in this work. Actually, we had no adequate means to estimate it. For example, conventional osmometry did not seem adaptable to our polymer fractions, because their number-average molecular weights were supposed to be quite high. No conventional solvent was applicable for their examination by gel-permeation chromatography. For these and other reasons we had to be content with leaving all the measured values uncorrected for polydispersity. Apparently, this fact makes the above-stated conclusions less definitive.

As a tentative attempt and as sometimes done we assume that correction of $\langle S^2\rangle$ for polydispersity is the most crucial among others and design a 10% reduction to convert the observed z average $\langle S^2\rangle^{1/2}$ to weight average values. Then our observed values of Ψ, Φ, and Φ_0 are raised approximately by 30%, but those of α_s, α_η, and z remain unchanged. Thus if the major polydispersity correction is restricted to $\langle S^2\rangle$, conclusions (1) and (3) stated above hold as they stand.

Acknowledgment. The authors wish to thank Professor M. Kurata of Kyoto University and Professor H. Utiyama of Hiroshima University, who kindly lent them the rotational viscometer used in this study. They also acknowledge the assistance of Mr. T. Mitani of this laboratory, who prepared the PMPL samples used, and the advice of Mr. M. Iida and Mr. Y. Fukumori of Osaka University in the synthesis of PMPL and PHB.

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(23) Figure 10 suggests that, for $\alpha_s^2 > 3$, plots of α_s^2 vs. $M^{1/5}$ are fitted by a straight line through the origin and that the slope of the line may be equated to $1.55(3/2\pi)^{3/5}(B/A3)^{2/5}$. This fact may be conveniently used to estimate B and β.

Chain Transfer in Radical Polymerizations and End Group Content of Resultant Polymers

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ABSTRACT: The radical polymerization of vinyl monomers was carried out in the presence of reactive chain transfer agents possessing functional groups and the weight fractions of the resultant polymers bearing functional groups from the transfer agents were determined with a thin-layer chromatographic method. The monomer–chain-transfer agent combination chosen in the present work is styrene–trichloroacetyl chloride and methyl methacrylate–2-aminoethanethiol hydrochloride. The chain-transfer polymerizations were expected to produce polystyrene with an acyl chloride end group and poly(methyl methacrylate) with an amino end group in a high yield. The end group content of resultant polymers determined by the thin-layer chromatography was in both cases in good agreement with that predicted from the polymerization kinetics, suggesting that the thin-layer chromatography can be effectively applied to the end group determination.

When transfer reaction takes place to an added chain-transfer agent, each transfer causes one molecule of the transfer agent to become incorporated in polymer.[1] Although factors influencing the chain transfer and effects of the chain-transfer agent on reduction in polymer chain length have been extensively investigated, there have been published few papers[2,3] which analyze the content of transfer agent fragments based on kinetics of the transfer reaction, except for the telomerization. This may be due to a lack of methods sensitive to the end group determination of polymers with relatively high molecular weight. It seems of interest to examine the applicability for determining the end group content of the thin-layer chromatography which is becoming a powerful tool in polymer characterizations.

The objects of the present study on radical polymerizations in the presence of chain-transfer agents are determination of the end groups of the resultant polymer by thin-layer chromatography, comparison of the end group content with the theoretical values from the kinetic treatment, and preparation of polymers bearing terminal functional groups to be used for polymer–polymer coupling reactions.

This paper describes a radical polymerization of styrene in the presence of trichloroacetyl chloride (TCAC) and that of methyl methacrylate (MMA) in the presence of 2-aminoethanethiol hydrochloride (AET·HCl). Both are reported to be reactive chain-transfer agents.[4,5] It is expected that polystyrene (PS) with an acyl chloride end group and PMMA with an amino end group will be produced as a result of these chain-transfer polymerizations.

Experimental Section

Reagents. Styrene and MMA monomers were purified by the conventional method. 2-Aminoethanethiol (AET) was synthesized in our laboratory from ethyleneimine and hydrogen sulfide[6] and purified by sublimation immediately before use. AET·HCl was obtained by addition of hydrochloric acid to AET in an aqueous solution. TCAC and other reagents were all commercial materials, which were purified by distillation before use.

Polymerization. Styrene–TCAC mixtures containing a given quantity of 2,2′-azobis(isobutyronitrile) (AIBN) as initiator were degassed by a freezing–thawing cycle and sealed under a pressure of 10^{-5} mm of Hg. In the case of MMA–AET·HCl, methanol was added to the monomer mixtures by 50 vol % to dissolve the proper amount of AET·HCl in MMA and then degassed without freezing. In both cases polymerization was carried out at 60 °C until a maximum of 10% conversion had taken place. After the polymerization, the contents were poured into plenty of methanol to precipitate the polymers. By the contact with methanol the acyl chloride end groups attached to PS molecules were directly converted to methyl ester. On the other hand, a portion of styrene polymerization mixtures was evaporated to dryness and the polymer was dissolved in dioxane followed by addition of water by 50% to convert the acyl chloride into carboxyl groups. The styrene and MMA polymers were purified by repeated precipitation from their solutions and dried at reduced pressure to a constant weight. The rate of polymerization was deduced from the weight of the polymer formed.

The number average degrees of polymerization $\overline{P}_n$ of the polymers were determined from intrinsic viscosities at 25 °C using the following equations derived with osmometry.

$$[\eta] = 33.5 \times 10^{-4}\overline{P}^{0.73} \quad \text{(PS, in benzene)}^{7} \qquad (1)$$

$$[\eta] = 17.3 \times 10^{-4}\overline{P}^{0.71} \quad \text{(PMMA, in acetone)}^{8} \qquad (2)$$

Thin-Layer Chromatography. Silica gels precoated to a thickness of 0.25 mm on glass plates were used for the thin-layer chromatography. The coated gel was washed by developing with methanol followed by activating at 110 °C for 1 h just prior to use. A chloroform solution (10 μL of 0.1%) of polymer was deposited on the plate and then the development was done at room temperature with benzene for PS and with ethyl acetate for PMMA. For comparison, the thin-layer chromatography was also carried out for the polymers after converting their polar end groups COOH and NH_2·HCl to $COOCH_3$ and $NHCOCH_3$, respectively. The weight fraction of polymers carrying the polar end groups was determined by densitometry of the chromatograms after staining the developed (upper spot, $R_f = 1$) and undeveloped (lower spot, $R_f = 0$) portions with 10% perchloric acid aqueous solution for PS and 10% methanol solution of I_2 for PMMA. Transmitted white light was used for the densitometry of PS and reflected light with a scanning wavelength of 420 nm for that of PMMA.

Results and Discussion

Equations Necessary to Evaluate the Number of Transfer Agent Fragments per Polymer Molecule. The polymerization of vinyl monomers in the presence of chain-transfer agent SX would give rise to formation of three kinds of polymer which are different in the number of the transfer agent fragments X attached to the chain ends. In the present chain-transfer polymerizations X must have a reactive functional group: acyl chloride or amino group. The polymer with terminal X groups at both chain ends will be designated as XPX, the polymer with a terminal X at one chain end as PX, and the polymer without terminal X as P. The weight fractions of each polymer type, w_{XPX}, w_{PX}, and w_P, can be calculated, provided that the polymerization involves the following elementary reactions which are conventionally accepted.

$$\mathrm{I} \rightarrow 2\mathrm{I}\cdot \qquad \text{(i)}$$

Initiation R_i

$$\mathrm{I}\cdot + \mathrm{M} \rightarrow \mathrm{M}\cdot \qquad \text{(ii)}$$

Propagation

$$\mathrm{M}\cdot + \mathrm{M} \rightarrow \mathrm{M}\cdot \qquad k_p[\mathrm{M}\cdot][\mathrm{M}] \qquad \text{(iii)}$$

$$\mathrm{XM}\cdot + \mathrm{M} \rightarrow \mathrm{XM}\cdot \qquad k_p[\mathrm{XM}\cdot][\mathrm{M}] \qquad \text{(iv)}$$

Chain transfer

$$\mathrm{M}\cdot + \mathrm{SX} \rightarrow \mathrm{P} + \mathrm{X}\cdot \qquad k_{tr}[\mathrm{M}\cdot][\mathrm{SX}] \qquad \text{(v)}$$

$$\mathrm{XM}\cdot + \mathrm{SM} \rightarrow \mathrm{PX} + \mathrm{X}\cdot \qquad k_{tr}[\mathrm{XM}\cdot][\mathrm{SX}] \qquad \text{(vi)}$$

Reinitiation

$$\mathrm{X}\cdot + \mathrm{M} \rightarrow \mathrm{XM}\cdot \qquad k_1[\mathrm{X}\cdot][\mathrm{M}] \qquad \text{(vii)}$$

Termination

$$\mathrm{M}\cdot + \mathrm{M}\cdot \rightarrow \mathrm{P} + \mathrm{P} \qquad k_{t,d}[\mathrm{M}\cdot]^2 \qquad \text{(viii)}$$

$$\mathrm{M}\cdot + \mathrm{M}\cdot \rightarrow \mathrm{P} \qquad k_{t,c}[\mathrm{M}\cdot]^2 \qquad \text{(ix)}$$

$$\mathrm{XM}\cdot + \mathrm{M}\cdot \rightarrow \mathrm{PX} + \mathrm{P} \qquad k_{t,d}[\mathrm{XM}\cdot][\mathrm{M}\cdot] \qquad \text{(x)}$$

$$\mathrm{XM}\cdot + \mathrm{M}\cdot \rightarrow \mathrm{PX} \qquad k_{t,c}[\mathrm{XM}\cdot][\mathrm{M}\cdot] \qquad \text{(xi)}$$

$$\mathrm{XM}\cdot + \mathrm{XM}\cdot \rightarrow \mathrm{PX} + \mathrm{PX} \qquad k_{t,d}[\mathrm{XM}\cdot]^2 \qquad \text{(xii)}$$

$$\mathrm{XM}\cdot + \mathrm{XM}\cdot \rightarrow \mathrm{XPX} \qquad k_{t,c}[\mathrm{XM}\cdot]^2 \qquad \text{(xiii)}$$

$$\mathrm{M}\cdot + \mathrm{X}\cdot \rightarrow \mathrm{PX} \qquad k_2[\mathrm{M}\cdot][\mathrm{X}\cdot] \qquad \text{(xiv)}$$

$$\mathrm{XM}\cdot + \mathrm{X}\cdot \rightarrow \mathrm{XPX} \qquad k_2[\mathrm{XM}\cdot][\mathrm{X}\cdot] \qquad \text{(xv)}$$

$$\mathrm{X}\cdot + \mathrm{X}\cdot \rightarrow \mathrm{X{-}X} \qquad k_3[\mathrm{X}\cdot]^2 \qquad \text{(xvi)}$$

In this scheme the symbols have the conventional meaning and transfer reactions to monomer, polymer, initiator, and methanol were all neglected because of their low possibility compared with that to the added transfer agents. The last three reactions xiv–xvi are involved to account for the reduction in overall rate of polymerization.

As will be discussed later, the present thin-layer chromatography cannot distinguish between PX and XPX but between P and (PX + XPX) and hence enables the determination of the w_P value. Considering that the polymer *P* is produced through the reactions v, viii, ix, or x, we can derive the expression for the w_P as a function of the concentrations of the monomer [M] and the chain-transfer agent [SX], eq 3,

$$w_P = \frac{(R_ik_t)^{1/2}[\{(k_1k_t/k_2)[\mathrm{M}] + k_{tr}[\mathrm{SX}] + (R_ik_t)^{1/2}\}\{k_{tr}[\mathrm{SX}](k_{tr}[\mathrm{SX}] + (R_ik_t)^{1/2}) + R_ik_t\} + (\lambda k_1k_tk_{tr}/k_2)[\mathrm{SX}][\mathrm{M}](R_ik_t)^{1/2}]}{\{k_{tr}[\mathrm{SX}] + (R_ik_t)^{1/2}\}^3\{(k_1k_t/k_2)[\mathrm{M}] + (R_ik_t)^{1/2}\}} \qquad (3)$$

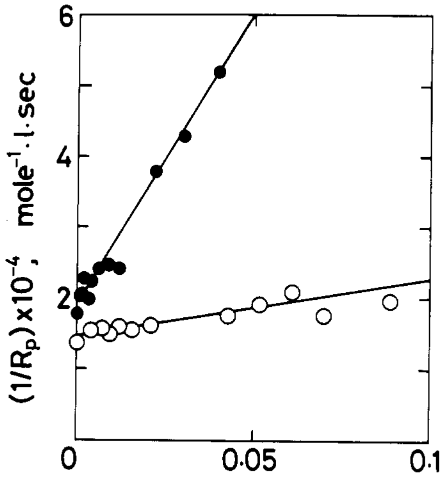

Figure 1. Overall rates of polymerization R_p in styrene–trichloroacetyl chloride and MMA–2-aminoethanethiol hydrochloride polymerizations at 60 °C: (○) styrene ([AIBN] = 8.72×10^{-3} mol L^{-1}); (●) MMA ([AIBN] = 1.42×10^{-3} mol L^{-1}, [methanol] = 50 vol %); (—) calculated according to eq 4 with kinetic data.

where k_t and λ are ($k_{t,d} + k_{t,c}$) and $k_{t,d}/k_t$, respectively. The derivation of eq 3 is given in Appendix A, together with that for w_{PX} and w_{XPX}. In the derivation, k_2 is assumed to be equal to $(k_3k_t)^{1/2}$ as Allen and co-workers postulated.[9]

Among the rate constants in eq 3, k_p, $k_{t,c}$, and $k_{t,d}$ have been reported, and R_i is also available if such an initiator is used as the decomposition rate constant k_d and the initiator efficiency f is known. Other rate constants, k_{tr}, k_1, and k_2, can be evaluated from R_p and $\overline{P}_n$ which are represented by

$$\frac{1}{R_p} = \frac{k_{tr}}{k_p(R_i/k_t)^{1/2}\{(R_ik_t)^{1/2} + (k_1k_t/k_2)[M]\}} \cdot \frac{[X]}{[M]} + \frac{1}{k_p[M](R_i/k_t)^{1/2}} \qquad (4)$$

$$\frac{1}{\overline{P}_n} = \frac{1}{\overline{P}_{n,o}} + \frac{k_{tr}}{k_p} \cdot \frac{[SX]}{[M]} \times \left[1 + \frac{(1-\lambda)(R_ik_t)^{1/2}}{2\{(k_1k_t/k_2)[M] + k_{tr}[SX] + (R_ik_t)^{1/2}\}}\right] \qquad (5)$$

$$\frac{1}{\overline{P}_{n,o}} = \frac{(1+\lambda)(R_ik_t)^{1/2}}{2k_p[M]} \qquad \left(\text{for } \frac{[SX]}{[M]} = 0\right) \qquad (6)$$

These equations are derived from the above polymerization scheme (see Appendix A). Strictly, one cannot know separatedly the values of k_1 and k_2 but merely the ratio k_1/k_2. It is of interest to note that the well-known Mayo's linear relation between $1/\overline{P}_n$ and [SX]/[M] is realized only when λ is unity or k_2 is zero.

Equations 3–6 are valid for the generalized polymerization. If the transfer reaction is not of degradative type, that is, the reactions xiv–xvi can be neglected, the kinetic expressions become simple. In addition, the weight fractions w_P of polymers carrying no terminal functional groups X can be expressed as a function of $\overline{P}_n$ or $\overline{P}_{n,o}/\overline{P}_n$ (=r) as follows:

$$w_P = \frac{2[\{(1+\lambda)(r-1)+2\}^3 + 2(\lambda^2-1)(r-1)]}{(1+\lambda)(r-1)+2^3} \qquad (7)$$

The derivation is given in Appendix B. Therefore, one can calculate w_P only from the data on $\overline{P}_n$, if the transfer reaction is assumed to be not of degradative type.

Polymerization. The reciprocals of the overall rate of polymerization and $\overline{P}_n$ are plotted against [SX]/[M] in Figures 1 and 2, respectively. The initial concentrations of AIBN are 8.72×10^{-3} mol L^{-1} for styrene and 1.42×10^{-3} mol L^{-1} for MMA. As can be seen, the linearity approximately holds between $1/R_p$ and [SX]/[M] as well as between $1/\overline{P}_n$ and [SX]/[M]. The evaluation of k_{tr} and k_1/k_2 from these results requires the knowledge of k_p, k_t, and λ. As it is known that the styrene polymerization terminates almost exclusively by coupling, while disproportionation is predominant in MMA,[10] we assume for simplicity λ to be zero for styrene and unity for MMA. This assumption can be applied without serious error, since the transfer reaction predominates in the present polymerizations. As for R_i, k_p, and k_t, we adopt the data of Matheson and co-workers for styrene[11] ($R_i = 1.47 \times 10^{-7}$ mol L^{-1} s^{-1}, $k_p = 176$ L mol^{-1} s^{-1}, and $k_t = 7.2 \times 10^7$ L mol^{-1} s^{-1}) and the data of O'Brien and Gornick for MMA[12] ($R_i = 1.38 \times 10^{-8}$ mol L^{-1} s^{-1}, $k_p = 573$ L mol^{-1} s^{-1}, and $k_t = 2.78 \times 10^7$ L mol^{-1} s^{-1}). By fitting these rate constants, and eq 4 and 5, to Figures 1 and 2, values of k_{tr} and k_1/k_2 were finally obtained. Full lines given in Figures 1 and 2 were drawn on the basis of eq 4 and 5 with a set of the following kinetic constants.

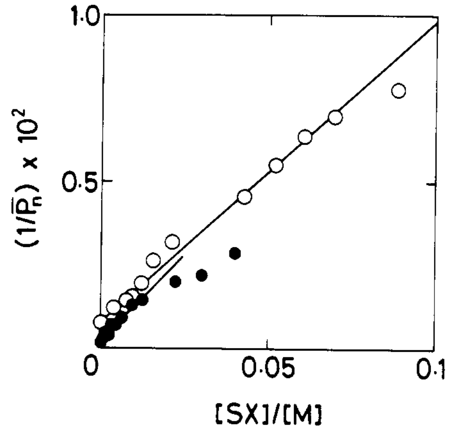

Figure 2. Number average degrees of polymerization $\overline{P}_n$ in styrene–trichloroacetyl chloride and MMA–2-aminoethanethiol hydrochloride polymerizations at 60 °C: (○) styrene ([AIBN] = 8.72×10^{-3} mol L^{-1}); (●) MMA ([AIBN] = 1.42×10^{-3} mol L^{-1}, [methanol] = 50 vol %); (—) calculated according to eq 5 with kinetic data.

Styrene–TCAC polymerization:

$$k_{tr} = 15.4 \text{ L mol}^{-1}\text{ s}^{-1}, \quad k_1/k_2 = 4.5 \times 10^{-8}$$

MMA–AET·HCl polymerization:

$$k_{tr} = 60.2 \text{ L mol}^{-1}\text{ s}^{-1}, \quad k_1/k_2 = 3.9 \times 10^{-8}$$

The chain-transfer constants C_s are then calculated to be 0.093 for styrene–TCAC and 0.11 for MMA–AET·HCl. The increase in $1/R_p$ with [SX]/[M] shown in Figure 1 indicates that styrene–TCAC and, particularly, MMA–AET·HCl accompany a degradative chain-transfer reaction in the polymerizations. The observed plots of $1/\overline{P}_n$ against [SX]/[M] are practically also in agreement with the theoretical curves which would be obtained in the case of nondegradative transfer reactions (the theoretical curves are not given in Figure 2 because of close overlapping with the full lines).

It is noteworthy that no appreciable chain-transfer reaction took place when free AET($HSC_2H_4NH_2$) was used as chain-transfer agent instead of hydrochloride salt of AET.

Thin-Layer Chromatography. Typical thin-layer chromatograms of PS specimen are given in Figure 3. (The darkness of the spots does not show up in the photograph well.) The symbols H and Me denote that the PS carries carboxyl and methyl ester end groups, respectively. $\overline{P}_n$ is 100 for sample 22 and 840 for sample 34. Sample 35 was obtained by polymerization at [SX]/[M] = 0 and has $\overline{P}_n$ of 1340. The chromatograms for 22-Me and 34-Me demonstrate that their rate of flow is the same as that of the developer, similar to the

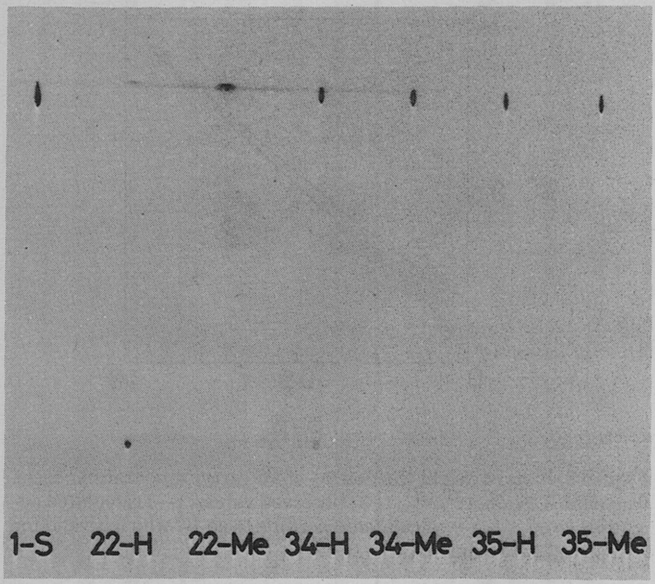

Figure 3. Examples of thin-layer chromatograms of PS specimen (gel, silica; developer, benzene; indicator, perchloric acid). See the text for the code of specimen.

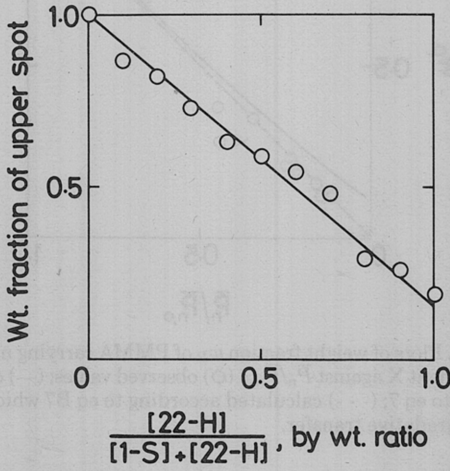

Figure 4. Weight fraction of upper spot in the thin-layer chromatogram determined by a densitometer for mixtures of a PS specimen (22-H) and the standard PS (1-S).

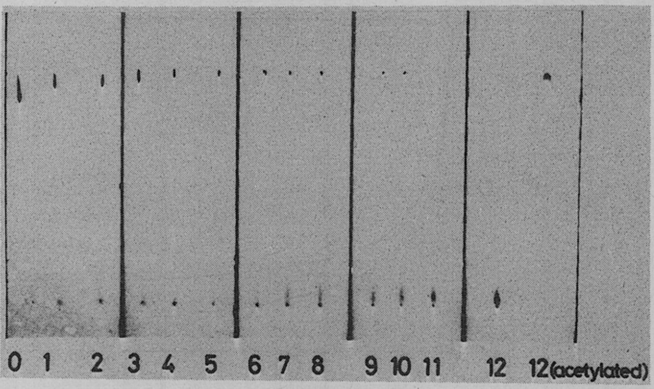

Figure 5. Thin-layer chromatograms of PMMA specimen (gel, silica; developer, ethyl acetate; indicator, I_2). The sample number corresponds to the [SX]/[M] mole ratio as follows: 0 (0); 1 (0.0005); 2 (0.001); 3 (0.002); 4 (0.003); 5 (0.004); 6 (0.006); 7 (0.009); 8 (0.012); 9 (0.016); 10 (0.022); 11 (0.036); 12 (0.040).

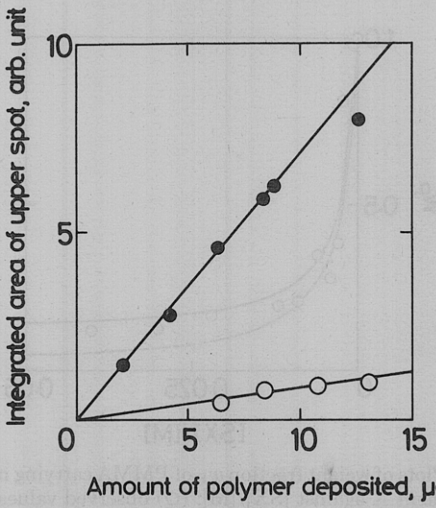

Figure 6. Relationship between the integrated area of upper spot and the amount of polymer deposited: (○) PMMA, sample number 11; (●) the standard PMMA.

standard PS from Pressure Chemical Co. (1-S) which bears no functional end group. In the case of 22-H and 34-H, however, a portion of polymers remains undeveloped on the deposited point, so that these polymers are identified to be a mixture of polymers with and without a functional group, the former being strongly adsorbed on the silica gel owing to the polar carboxyl group attached to the polymer. It is reasonable that no difference in the chromatogram is detected between 35-H and 35-Me, because these polymers, obtained by a polymerization without chain-transfer agent, have no functional end groups at all. The above results afford an evidence that at least a fraction of the intact PS molecules formed by the radical polymerization in the presence of TCAC carry an acyl chloride group at the chain end. It follows that the fraction of PS developed in the chromatogram should be exactly equal to the weight fraction w_P of PS carrying no functional end groups. To examine the accuracy of the densitometry, mixtures from 22-H and the standard PS (1-S) were applied to thin-layer chromatography. The result is given in Figure 4, where the ratio of amount of the polymer developed (upper spot in the chromatogram) to the sum of the amount of the polymer undeveloped (lower spot in the chromatogram) and developed is plotted against the weight fraction of 22-H in the polymer mixture. The good linearity found in Figure 4 indicates the densitometry to be feasible for the evaluation of the w_P.

Figure 5 shows the thin-layer chromatograms of all the PMMA specimen. The amount of each polymer deposited is 10 μg. The fraction of lower spot increases, as the sample number, i.e., [SX]/[M] in the polymerization mixture, becomes larger. This fact suggests that the MMA polymer has a larger content of polar functional end groups at a higher [SX]/[M] ratio. A strong evidence for the functional end group to be an amino group is provided by the chromatogram of the PMMA reacted with acetyl chloride prior to the chromatographic development, as is seen for the PMMA of No. 12 in Figure 5. The lower spot which is observed for the polymer before the reaction with acetyl chloride disappears as a consequence of blocking the amino group.

To determine the weight fraction of the polymer developed, the amount of the upper spot of PMMA was measured by a densitometer for varying amounts of the deposited polymer. One example is given in Figure 6, together with that for a standard PMMA possessing no amino group. The integrated area indicated by the densitometer is proportional to the amount of the deposited PMMA. The ratio of the slope of the linear curve for the PMMA specimen to that of the standard PMMA gives the w_P value.

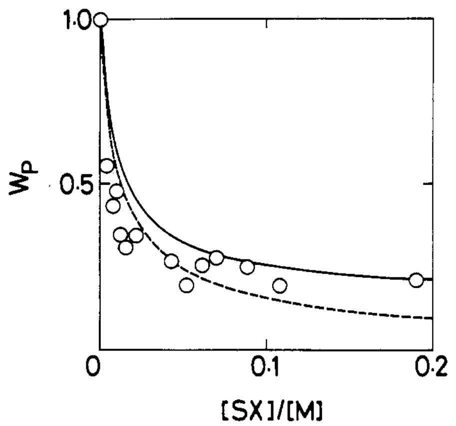

Figure 7. Plots of weight fraction w_P of PS carrying no transfer agent fragment X against [SX]/[M]: (○) observed values; (—) calculated according to eq 3; (- - -) calculated according to eq B1 which is valid for nondegradative transfer.

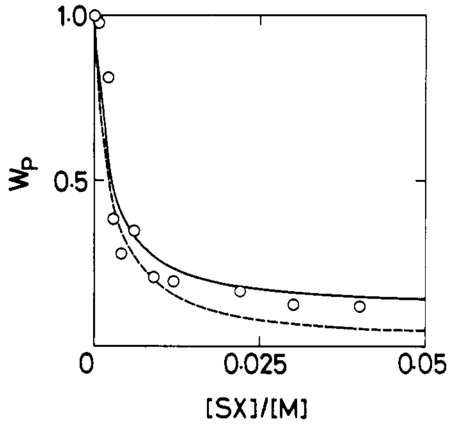

Figure 8. Plots of weight fraction w_P of PMMA carrying no transfer agent fragment X against [SX]/[M]: (○) observed values; (—) calculated according to eq 3; (- - -) calculated according to eq B1 which is valid for nondegradative transfer.

Comparison of Observed and Calculated w_P Values. As described earlier, the whole polymer must be a mixture of three kinds of polymer different in the number of functional end groups (P, PX, and XPX). Though we made an additional chromatographic experiment with other developers than benzene and ethyl acetate, it was not successful to separate distinctly PX and XPX, and we could determine merely the fraction of upper spot which corresponds to the fraction w_P of the polymer bearing no functional end group.

The observed w_P values are plotted against [SX]/[M] in Figure 7 for PS and in Figure 8 for PMMA. The solid curves represent the values calculated according to eq 3 with the kinetic data and the broken curves those calculated under the assumption of nondegradative transfer (eq B1 in Appendix B). Initially both the observed and calculated w_P fall off very rapidly as [SX]/[M] increases, but subsequently they flatten out. The observed values are close to those calculated within the limits of experimental error. As is apparent from Figures 9 and 10, a similar agreement between the observed and calculated values is seen in the plots of w_P against $\bar{P}_n/\bar{P}_{n,o}$. The theoretical curves for nondegradative transfer reaction are different from those for degradative transfer to an appreciable extent, but the reproducibility of the present chromatographic data was not good enough to indicate the transfer to be of degradative type. Inspection of Figures 7 to 10 leads to a conclusion that one may roughly estimate the w_P value from the theory which is valid for the nondegradative chain-transfer polymerization, even if the transfer reaction is of a degradative type.

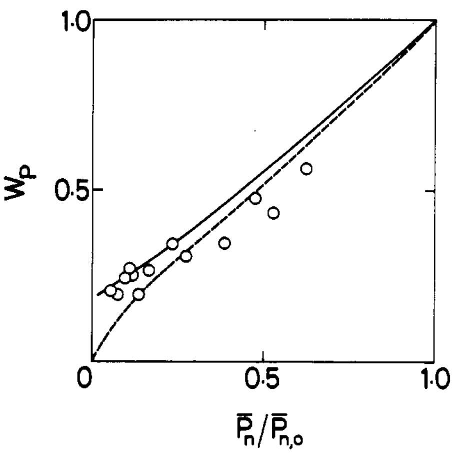

Figure 9. Plots of weight fraction w_P of PS carrying no transfer agent fragment X against $\bar{P}_n/\bar{P}_{n,o}$: (○) observed values; (—) calculated according to eq 7; (- - -) calculated according to eq B7 which is valid for nondegradative transfer.

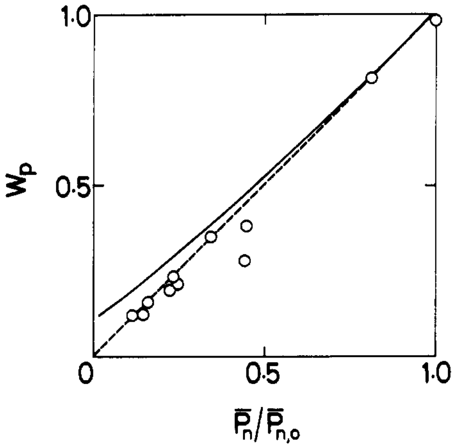

Figure 10. Plots of weight fraction w_P of PMMA carrying no transfer agent fragment X against $\bar{P}_n/\bar{P}_{n,o}$: (○) observed values; (—) calculated according to eq 7; (- - -) calculated according to eq B7 which is valid for nondegradative transfer.

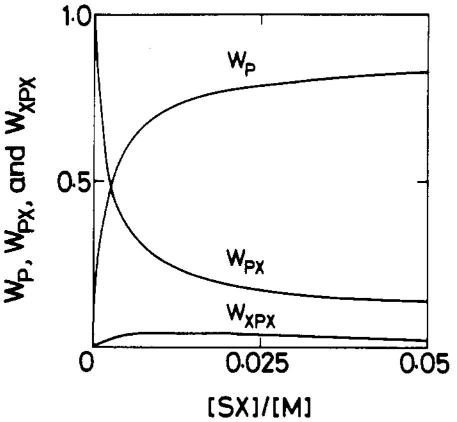

Figure 11. w_P, w_{PX}, and w_{XPX} values for PMMA calculated according to eq A10, A11, and A12.

It seems to be very difficult to determine experimentally the w_{PX} and w_{XPX}. Therefore, we estimated them with the use of eq A11 and A12 in Appendix A. The w_{PX} and w_{XPX} values, shown in Figure 11, were calculated for the MMA polymerization from the kinetic data under an assumption of disproportionation termination, similar to w_P. It is seen that

w_{XPX} amounts to a definite value, though much lower than the w_{PX}. According to the proposed polymerization scheme, the polymer XPX would result from the radical combination reaction xv between XP· and X·.

Finally, the distribution of the functional end groups in the polymer was studied with PMMA prepared at [SX]/[M] = 0.0109. This was fractionated into 11 fractions and the thin-layer chromatography was run on each fraction. In contrast to the finding of De Boos,[5] it was found that the fractions exhibited no significant difference in w_P.

The satisfactory agreement between the observed and calculated w_P suggests that the thin-layer chromatography proves to be a method feasible for determining a functional end group, even in the case that the molecular weight of the polymer is too high to be determined by the conventional chemical analytical method. For instance, the molecular weight of PMMA in Figure 8 is 2.5 × 10^5 at [SX]/[M] = 0.002 and 1.0 × 10^5 at [SX]/[M] = 0.006. Another advantage of the thin-layer chromatography is that this method does not require careful removal of all traces of adsorbed material from polymers prior to end group analysis. Recently Min and coworkers also have pointed out the usefulness of thin-layer chromatography for end group analysis.[13] However, it should be mentioned that the method of using thin-layer chromatography for end group analysis only works for polar end groups.

The above analysis is based on the assumtion that the polymerization proceeds through the elementary reactions i–xvi. However, there are alternative possibilities of chain transfer on trichloroacetyl chloride, as outlined below

$$\mathrm{M\cdot\ (or\ XM\cdot) + CCl_3COCl \rightarrow MCl + \cdot CCl_2COCl} \qquad \text{(xvii)}$$

$$\mathrm{\cdot CCl_2COCl + M \rightarrow XM\cdot} \qquad \text{(xviii)}$$

$$\mathrm{M\cdot\ (or\ XM\cdot) + CCl_3COCl \rightarrow MCl + CCl_3CO\cdot \rightarrow CCl_3\cdot + CO} \qquad \text{(xix)}$$

$$\mathrm{M\cdot\ (or\ XM\cdot) + CCl_3COCl \rightarrow MCOCl + CCl_3\cdot} \qquad \text{(xx)}$$

$$\mathrm{CCl_3\cdot + M \rightarrow CCl_3M\cdot} \qquad \text{(xxi)}$$

$$\mathrm{CCl_3M\cdot + CCl_3COCl \rightarrow CCl_3MCl + \cdot CCl_2COCl\ or\ CCl_3\cdot} \qquad \text{(xxii)}$$

The reactions xvii and xviii are identical to reactions v (or vi) and vii, respectively. If these can be taken into account, one might get a better fit for Figure 7. (This is, however, impossible in this case because of the additional rate constants for xix–xxii, which are not available in the present work.)

Coupling reactions of the polymers carrying these reactive end groups will be described in subsequent papers.

Acknowledgment. The authors are indebted to Professor Ichiro Sakurada for advice and encouragement throughout the course of this investigation.

Appendix A. Degradative Transfer

From the definition the weight fractions w_P, w_{PX}, and w_{XPX} can be expressed as eq A1–A3. If the usual steady-state assumptions with respect to the concentrations of radicals may be applied and k_2 is assumed to be equal to $(k_3k_t)^{1/2}$, the stationary radical concentrations [M·], [XM·], and [X·] can be obtained from eq A4–A6.

$$w_P = \frac{k_{tr}[M\cdot][SX] + \lambda k_t[M\cdot]^2 + \lambda k_t[XM\cdot][M\cdot] + (1-\lambda)k_t[M\cdot]^2}{k_{tr}[M\cdot][SX] + k_{tr}[XM\cdot][SX] + \lambda k_t([M\cdot] + [XM\cdot])^2 + (1-\lambda)k_t([M\cdot] + [XM\cdot])^2 + k_2[M\cdot][X\cdot] + k_2[XM\cdot][X\cdot]} \qquad \text{(A1)}$$

$$w_{PX} = \frac{k_{tr}[XM\cdot][SX] + \lambda k_t[XM\cdot][M\cdot] + 2(1-\lambda)k_t[XM\cdot][M\cdot] + \lambda k_t[XM\cdot]^2 + k_2[M\cdot][X\cdot]}{k_{tr}[M\cdot][SX] + k_{tr}[XM\cdot][SX] + \lambda k_t([M\cdot] + [XM\cdot])^2 + (1-\lambda)k_t([M\cdot] + [XM\cdot])^2 + k_2[M\cdot][X\cdot] + k_2[XM\cdot][X\cdot]} \qquad \text{(A2)}$$

$$w_{XPX} = \frac{(1-\lambda)k_t[XM\cdot]^2 + k_2[XM\cdot][X\cdot]}{k_{tr}[M\cdot][SX] + k_{tr}[XM\cdot][SX] + \lambda k_t([M\cdot] + [XM\cdot])^2 + (1-\lambda)k_t([M\cdot] + [XM\cdot])^2 + k_2[M\cdot][X\cdot] + k_2[XM\cdot][X\cdot]} \qquad \text{(A3)}$$

$$R_i = k_{tr}[M\cdot][SX] + k_t[M\cdot]^2 + k_t[XM\cdot][M\cdot] + k_2[M\cdot][X\cdot] \qquad \text{(A4)}$$

$$k_1[X\cdot][M] = k_{tr}[XM\cdot][SX] + k_t[XM\cdot][M\cdot] + k_t[XM\cdot]^2 + k_2[XM\cdot][X\cdot] \qquad \text{(A5)}$$

$$k_{tr}[M\cdot][SX] + k_{tr}[XM\cdot][SX] = k_1[X\cdot][M] + k_2[M\cdot][X\cdot] + k_2[XM\cdot][X\cdot] + (k_2^2/k_t)[X\cdot]^2 \qquad \text{(A6)}$$

Hence, the concentrations are given by eq A7–9.

$$[M\cdot] = \frac{R_i}{k_{tr}[SX] + (R_ik_t)^{1/2}} \qquad \text{(A7)}$$

$$[XM\cdot] = \frac{(k_1k_{tr}/k_2)(R_ik_t)^{1/2}[M][SX]}{\{k_{tr}[SX] + (R_ik_t)^{1/2}\}\{(k_1k_t/k_2)[M] + k_{tr}[SX] + (R_ik_t)^{1/2}\}} \qquad \text{(A8)}$$

$$[X\cdot] = \frac{(k_{tr}/k_2)(R_ik_t)^{1/2}[SX]}{(k_1k_t/k_2)[M] + k_{tr}[SX] + (R_ik_t)^{1/2}} \qquad \text{(A9)}$$

Substitution of these concentrations into eq A1–A3 leads to the following expressions (eq A10–A12) for each fraction as functions of the concentrations of the monomer [M] and the chain-transfer agent [SX].

$$w_P = \frac{(R_ik_t)^{1/2}[\{(k_1k_t/k_2)[M] + k_{tr}[SX] + (R_ik_t)^{1/2}\}\{k_{tr}[SX](k_{tr}[SX] + (R_ik_t)^{1/2}) + R_ik_t\} + (\lambda k_1k_tk_{tr}/k_2)[SX][M](R_ik_t)^{1/2}]}{\{k_{tr}[SX] + (R_ik_t)^{1/2}\}^3\{(k_1k_t/k_2)[M] + (R_ik_t)^{1/2}\}} \qquad \text{(A10)}$$

$$w_{PX} = \frac{k_{tr}[SX][\{k_{tr}[SX] + (R_ik_t)^{1/2}\}\{(k_1k_tk_{tr}/k_2)[SX][M] + R_ik_t\}\{(k_1k_t/k_2)[M] + k_{tr}[SX] + (R_ik_t)^{1/2}\} + (2-\lambda)R_ik_t(k_1k_t/k_2)[M]\{(k_1k_t/k_2)[M] + k_{tr}[SX] + (R_ik_t)^{1/2}\} + \lambda\{(k_1k_t/k_2)[M]\}^2k_{tr}[SX](R_ik_t)^{1/2}]}{\{k_{tr}[SX] + (R_ik_t)^{1/2}\}^3\{(k_1k_t/k_2)[M] + (R_ik_t)^{1/2}\}\{(k_1k_t/k_2)[M] + k_{tr}[SX] + (R_ik_t)^{1/2}\}} \qquad \text{(A11)}$$

$$w_{XPX} = 1 - w_P - w_{PX} = \frac{(k_1k_tk_{tr}^2/k_2)(R_ik_t)^{1/2}[M][SX]^2\{(1-\lambda)(k_1k_t/k_2)[M] + k_{tr}[SX] + (R_ik_t)^{1/2}\}}{\{k_{tr}[SX] + (R_ik_t)^{1/2}\}^3\{(k_1k_t/k_2)[M] + (R_ik_t)^{1/2}\}\{(k_1k_t/k_2)[M] + k_{tr}[SX] + (R_ik_t)^{1/2}\}} \qquad \text{(A12)}$$

According to the definition, R_p and $\overline{P}_n$ are represented by

$$\frac{1}{R_p} = \frac{1}{k_p[M]([M\cdot] + [XM\cdot])} \qquad \text{(A13)}$$

$$\frac{1}{\overline{P}_n} = \frac{R_{tr} + R_t}{R_p}$$
$$= \frac{k_{tr}[M\cdot][SX] + k_{tr}[XM\cdot][SX] + \lambda k_t([M\cdot] + [XM\cdot])^2 + \{(1-\lambda)/2\}k_t([M\cdot] + [XM\cdot])^2 + k_2[M\cdot][X\cdot] + k_2[XM\cdot][X\cdot]}{k_p[M]([M\cdot] + [XM\cdot])} \quad \text{(A14)}$$

where R_t and R_{tr} are the rate of termination and transfer, respectively. Substituting the concentrations given by eq A7–A9 into eq A13 and A14, one obtains eq 4, 5, and 6.

Appendix B. Nondegradative Transfer

When the transfer reaction can be regarded nondegradative, we can discard reactions xiv–xvi in the polymerization scheme. Thus the limit $k_2 = 0$ in eq A10–A12 gives the values of w_P, w_{PX}, w_{XPX} in the case of nondegradative transfer:

$$w_P = \frac{(R_ik_t)^{1/2}\{k_{tr}[SX] + (R_ik_t)^{1/2}\}^2 + (\lambda - 1)k_{tr}[SX]R_ik_t}{\{k_{tr}[SX] + (R_ik_t)^{1/2}\}^3} \quad \text{(B1)}$$

$$w_{PX} = \frac{k_{tr}^2[SX]^2\{(1+\lambda)(R_ik_t)^{1/2} + k_{tr}[SX]\} + (2-\lambda)k_{tr}[SX]R_ik_t}{\{k_{tr}[SX] + (R_ik_t)^{1/2}\}^3} \quad \text{(B2)}$$

$$w_{XPX} = \frac{(1-\lambda)k_{tr}^2[SX]^2(R_ik_t)^{1/2}}{\{k_{tr}[SX] + (R_ik_t)^{1/2}\}^3} \quad \text{(B3)}$$

In addition, these weight fractions can be expressed as a function of $\overline{P}_n$ of the polymer, if the transfer occurs nondegradatively. In this case the stationary concentrations of [M·] and [XM·] are readily shown to be

$$[M\cdot] = \frac{R_i}{k_{tr}[SX] + (R_ik_t)^{1/2}} \quad \text{(B4)}$$

$$[XM\cdot] = \frac{k_{tr}[SX](R_ik_t)^{1/2}}{k_tk_{tr}[SX] + k_t(R_ik_t)^{1/2}} \quad \text{(B5)}$$

Since w_P is given by

$$w_P = \frac{k_{tr}[M\cdot][SX] + k_t[M\cdot]^2 + \lambda k_t[XM\cdot][M\cdot]}{k_{tr}[SX]([M\cdot] + [XM\cdot]) + k_t([M\cdot] + [XM\cdot])^2} \quad \text{(B6)}$$

substitution of eq B4 and B5 into eq B6 leads to

$$w_P = \frac{2[\{(1+\lambda)(r-1) + 2\}^2 + 2(\lambda^2 - 1)(r-1)]}{\{(1+\lambda)(r-1) + 2\}^3} \quad \text{(B7)}$$

where r is $\overline{P}_{n,o}/\overline{P}_n$. $\overline{P}_{n,o}$ denotes $\overline{P}_n$ of the polymer generated by polymerization in the absence of chain-transfer agent. Similarly, one can get

$$w_{PX} = \frac{(1+\lambda)^3(r+1)(r-1)^2 + 4(2-\lambda)(1+\lambda)(r-1)}{\{(1+\lambda)(r-1) + 2\}^3} \quad \text{(B8)}$$

$$w_{XPX} = \frac{2(1-\lambda)(1+\lambda)^2(1-r)^2}{\{(1+\lambda)(r-1) + 2\}^3} \quad \text{(B9)}$$

The thin-layer chromatography provides the weight fractions, while the end group determinations by conventional chemical analysis give us the number fractions. Therefore, it seems also important to derive the expressions for each number fraction x_P, x_{PX}, and x_{XPX}. Considering that these fractions are represented by eq B10–B12 and through the algebraic manipulation similar to w_P, w_{PX}, and w_{XPX}, we finally find the following expressions (eq B13–B15) as functions of [M] and [SX], and as a function of r ($= \overline{P}_{n,o}/\overline{P}_n$):

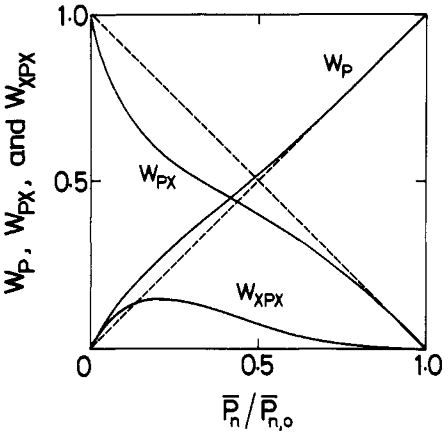

Figure 12. w_P, w_{PX}, and w_{XPX} values in the case of nondegradative transfer as a function of $\overline{P}_n/\overline{P}_{n,o}$: (—) $\lambda = 0$ (coupling termination); (- - -) $\lambda = 1$ (disproportionation termination).

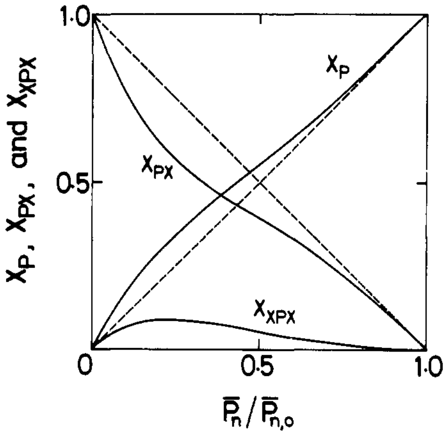

Figure 13. x_P, x_{PX}, and x_{XPX} values in the case of nondegradative transfer as a function of $\overline{P}_n/\overline{P}_{n,o}$: (—) $\lambda = 0$ (coupling termination); (- - -) $\lambda = 1$ (disproportionation termination).

$$x_P = \frac{(R_ik_t)^{1/2}\{k_{tr}^2[SX]^2 + (1+\lambda)k_{tr}[SX](R_ik_t)^{1/2} + \tfrac{1}{2}(1+\lambda)R_ik_t\}}{\{k_{tr}[SX] + (R_ik_t)^{1/2}\}^2\{k_{tr}[SX] + \tfrac{1}{2}(1+\lambda)(R_ik_t)^{1/2}\}} \quad \text{(B13)}$$

$$x_{PX} = \frac{k_{tr}[SX][\{k_{tr}[SX] + (R_ik_t)^{1/2}\}^2 + (\lambda - 1)k_{tr}[SX](R_ik_t)^{1/2}]}{\{k_{tr}[SX] + (R_ik_t)^{1/2}\}^2\{k_{tr}[SX] + \tfrac{1}{2}(1+\lambda)(R_ik_t)^{1/2}\}} \quad \text{(B14)}$$

$$x_{XPX} = \frac{\tfrac{1}{2}(1-\lambda)k_{tr}^2[SX]^2(R_ik_t)^{1/2}}{\{k_{tr}[SX] + (R_ik_t)^{1/2}\}^2\{k_{tr}[SX] + \tfrac{1}{2}(1+\lambda)(R_ik_t)^{1/2}\}} \quad \text{(B15)}$$

$$x_P = \frac{2\{(1+\lambda)(r^2-1) + 2\}}{r\{(1+\lambda)(r-1) + 2\}^2} \quad \text{(B16)}$$

$$x_P = \frac{k_{tr}[M\cdot][SX] + \lambda k_t[M\cdot]^2 + \tfrac{1}{2}(1-\lambda)k_t[M\cdot]^2 + \lambda k_t[XM\cdot][M\cdot]}{k_{tr}[M\cdot][SX] + k_{tr}[XM\cdot][SX] + \lambda k_t([M\cdot] + [XM\cdot])^2 + \tfrac{1}{2}(1-\lambda)k_t([M\cdot] + [XM\cdot])^2} \quad \text{(B10)}$$

$$x_{PX} = \frac{k_{tr}[XM\cdot][SX] + \lambda k_t[XM\cdot][M\cdot] + (1-\lambda)k_t[M\cdot][XM\cdot] + \lambda k_t[XM\cdot]^2}{k_{tr}[M\cdot][SX] + k_{tr}[XM\cdot][SX] + \lambda k_t([M\cdot] + [XM\cdot])^2 + \tfrac{1}{2}(1-\lambda)k_t([M\cdot] + [XM\cdot])^2} \quad \text{(B11)}$$

$$x_{XPX} = \frac{\tfrac{1}{2}(1-\lambda)k_t[XM\cdot]^2}{k_{tr}[M\cdot][SX] + k_{tr}[XM\cdot][SX] + \lambda k_t([M\cdot] + [XM\cdot])^2 + \tfrac{1}{2}(1-\lambda)k_t([M\cdot] + [XM\cdot])^2} \quad \text{(B12)}$$

$$x_{\mathrm{PX}} = \frac{(r-1)[\{(1+\lambda)(r-1)+2\}^2 - 2(1-\lambda^2)(r-1)]}{r\{(1+\lambda)(r-1)+2\}^2} \tag{B17}$$

$$x_{\mathrm{XPX}} = \frac{(1-\lambda^2)(r-1)^2}{r\{(1+\lambda)(r-1)+2\}^2} \tag{B18}$$

The dependence of each fraction on $\overline{P}_{\mathrm{n}}/\overline{P}_{\mathrm{n,o}}$ is given in Figures 12 and 13 for the cases of $\lambda = 0$ and 1. As is apparent from eq B9 and B18, the w_{XPX} and x_{XPX} values vanish when $\lambda = 1$ (disproportionation termination).

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Block Lengths of Step Copolymers formed by Coupling Identical Comonomer Functional Groups of Differing Reactivity

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Received May 31, 1977

ABSTRACT: Step copolymers formed by linking together comonomers of the type A_1–R_1–A_1 and A_2–R_2–A_2 in which A_1 and A_2 are identical functional groups having differing coupling reactivities due to the presence of R_1 or R_2 are predicted to form block copolymers. Number average block lengths are calculated by assuming the copolymerization to pass through three sequential stages: (1) self-coupling between the more reactive functional groups, A_1, (2) cross-coupling between the more and less reactive functional groups, and (3) self-coupling between the less reactive functional groups, A_2. The iterations required by the calculation may be circumvented by assuming the extent of conversion where the comonomers are polymerizing at an equal rate closely corresponds to the point where the more reactive monomer has attained its maximum number average block length. Numerical results based on assumed reactivity ratios show the block length to increase with an increasing difference in reactivity ratios. When both reactivity ratios are between 0 and 1, an azeotrope is predicted.

Most step polymerizations occur by the linking together of different functional groups (i.e., an acid and an alcohol) of bifunctional monomers. However, coupling reactions are known where functional groups of the same identity link together. Such an example, which has been employed as a polymerization system,[2] is the copper–amine catalyzed oxidative coupling of terminal diynes.

$$n\mathrm{HC{\equiv}CRC{\equiv}CH} \xrightarrow[\text{amine}]{\text{Cu}} \mathrm{H(-C{\equiv}CRC{\equiv}C-)}_n\mathrm{H} + (2n-2)\mathrm{H}^+$$

A particularly interesting consequence of the functional groups having the same identity is the absence of a stoichiometric restriction for obtaining high polymer. In a copolymerization the identity of R can be varied such that the coupling reactivity of the comonomer functional groups is different.

$$\mathrm{A_1{-}R_1{-}A_1} + \mathrm{A_2{-}R_2{-}A_2} \rightarrow [(-\mathrm{A_1{-}R_1{-}A_1}-)_p(-\mathrm{A_2{-}R_2{-}A_2}-)_q]_n$$

From cross-coupling experiments with the acetylenic coupling system,[3] it has been shown that the identity of R can have a substantial effect on the reactivity of A. It would be expected in a copolymerization system that the coupling would pass through three stages: first where coupling is predominant between the more reactive functional groups followed by cross-coupling and finally where coupling is predominant between the less reactive functional groups. The copolymer chain would then be expected to consist of block sequences of the comonomers. The present objective is to derive an equation for predicting number average block lengths and to obtain numerical results for a range of coupling reactivity differences.

Computation

In a step copolymer system where identical functional groups of the same and differing reactivities can couple to form polymer, three possible kinds of linkages may be formed: (1) a self-coupling between the monomers possessing the more reactive functional groups, (2) a cross-coupling between comonomers, and (3) a self-coupling between the monomers possessing the less reactive functional groups. These three reactions may be represented as follows

$$\mathrm{A_1} + \mathrm{A_1} \xrightarrow{k_{11}} \mathrm{P(A_1A_1)} \tag{1}$$

$$\mathrm{A_1} + \mathrm{A_2} \xrightarrow{k_{12}} \mathrm{P(A_1A_2)} \tag{2}$$

$$\mathrm{A_2} + \mathrm{A_2} \xrightarrow{k_{22}} \mathrm{P(A_2A_2)} \tag{3}$$

where A_1 is the more reactive functional group, A_2 is the less reactive functional group, and $\mathrm{P}(A_nA_n)$ is a polymer of DP $\geqslant 2$.