Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Quasiliving Carbocationic Polymerization. IV. Polymerization of p-tert-Butylstyrene

Judit Puskás[ab]; Gabor Kaszás[ac]; J. P. Kennedy[a]; T. Kelen[ac]; Ferenc Tüdös[d]
[a] Institute of Polymer Science, The University of Akron, Akron, Ohio [b] Technical Research Institute for Electronics, Budapest, Hungary [c] Central Research Institute for Chemistry, Hungarian Academy of Sciences, Budapest, Hungary [d] Central Research Institute for Chemistry Hungarian Academy of Sciences, Budapest, Hungary

To cite this Article Puskás, Judit , Kaszás, Gabor , Kennedy, J. P. , Kelen, T. and Tüdös, Ferenc(1982) 'Quasiliving Carbocationic Polymerization. IV. Polymerization of p-tert-Butylstyrene', Journal of Macromolecular Science, Part A, 18: 9, 1245 — 1261
To link to this Article: DOI: 10.1080/00222338208077221
URL: http://dx.doi.org/10.1080/00222338208077221

J. MACROMOL. SCI.–CHEM., A18(9), pp. 1245-1261 (1982-83)

Quasiliving Carbocationic Polymerization. IV. Polymerization of p-tert-Butylstyrene

JUDIT PUSKÁS,* GABOR KASZÁS,† J. P. KENNEDY, and T. KELEN†

Institute of Polymer Science
The University of Akron
Akron, Ohio 44325

FERENC TÜDŐS

Central Research Institute for Chemistry
Hungarian Academy of Sciences
1525 Budapest, Hungary

ABSTRACT

The mechanism of polymerization of p-tert-butylstyrene (ptBuSt) initiated by the cumyl chloride/BCl_3 initiating system in CH_2Cl_2 at -50°C has been investigated. At and below ~0.4 M ptBuSt, quasiliving polymerizations proceed, i.e., initiation is instantaneous, termination is absent or reversible, and chain transfer to monomer can be suppressed or eliminated. In the quasiliving range the $\overline{M}_n$ versus $[\text{ptBuSt}]_0$ plot is linear and passes through the origin, and $\overline{M}_w/\overline{M}_n$ decreases much below 2.0 with decreasing [ptBuSt]. GPC traces change from broad

---

*Visiting scientist. Permanent address: Technical Research Institute for Electronics, Budapest, Hungary.

†Visiting scientist. Permanent address: Central Research Institute for Chemistry, Hungarian Academy of Sciences, 1525 Budapest, Hungary.

multimodal to narrow monomodal and the color of polymerization charges change from colorless to golden-yellow with decreasing [ptBuSt]. The effect of temperature jump subsequent to monomer addition has been examined; however, it does not explain the peculiar monomer concentration effect on the mechanism. Changes in the ionicity may be responsible for this phenomenon.

INTRODUCTION

Recently it has been discovered [1] that under well-defined conditions, i.e., by the use of continuous steady slow monomer addition to efficient cationic initiating systems, the $\overline{M}_n$ of α-methylstyrene increases linearly with the amount of consumed monomer. This system exhibits features similar to living polymerizations, i.e., initiation is virtually instantaneous upon monomer addition, termination is absent or reversible, and chain transfer to monomer is virtually absent or largely suppressed over a reasonably wide range of conditions. To emphasize the similarity between these characteristics and those exhibited by truly living systems (i.e., in systems where $R_i \gg R_p$, $R_t = 0$, $R_{tr} = 0$), the term quasiliving was introduced [1].

Subsequent to the discovery of quasiliving cationic polymerization of α-methylstyrene [1], intensive reasearch has been carried out to find other monomers that behave similarly. These efforts have been successful and quasiliving carbocationic polymerizations have been defined to exist, for example, with isobutylene [2], styrene [3], isobutyl vinyl ether [4], and methyl vinyl ether [5].

In the course of experimentation aimed to extend the scope and to gain insight into the fundamentals of quasiliving cationic polymerizations, it was of interest to elucidate the polymerization behavior of p-t-butylstyrene (ptBuSt). During these studies a series of surprising phenomena have been observed which prompted us to undertake a detailed investigation on the effect of monomer concentration on the polymerization of ptBuSt. This paper concerns the mechanism of ptBuSt polymerization, particularly the changes that occur at low monomer concentrations and the definition of conditions under which quasiliving polymerization of ptBuSt can be achieved.

EXPERIMENTAL PART

Materials

p-t-Butylstyrene and α-methylstyrene were extracted with 10% aqueous NaOH, washed neutral with distilled water, dried over molecular sieves (3Å), and distilled from CaH_2 under vacuum. Methylene chloride was purified as described [6]. BCl_3 was condensed from a lecture bottle under N_2. Cumyl chloride (2-chloro-2-phenylpropane, CC) was prepared from purified α-methylstyrene by hydrochlorination in methylene chloride solution; excess HCl and solvent were removed by repeated freeze-drying.

Procedures

Polymerizations by conventional technique (controls) were carried out in a stainless steel enclosure under dry N_2 at -50°C in capped culture tubes. The total volume of polymerization mixtures was 25 cm^3. The initial concentrations of BCl_3 and CC were 3.5×10^{-2} and 1.03×10^{-2} mol/dm^3, respectively. Polymerizations were stopped by adding methanol to the charge. Conversions were determined gravimetrically.

Polymerizations by continuous, slow, steady monomer addition were carried out in a stainless steel enclosure in 300 cm^3 three-neck round-bottom flasks equipped with stirrer, Teflon plug for monomer addition, and outlet for sampling under dry N_2 at -50°C. The initial volume of solvent was 100 cm^3 and the initial concentrations of BCl_3 and CC were 3.5×10^{-2} and 1.03×10^{-2} mol/dm^3, respectively. Monomer mixtures were fed continuously by a precision metering pump (Beckman Model 110A) through a precision glass capillary outlet. The temperature of the charge was measured by a thermocouple sealed into a thin glass tube placed directly into the charge. Samples (0.1 cm^3) were withdrawn with a syringe and were injected into capped vials containing excess methanol. Polymerizations were stopped by adding methanol to the charge. Conversions were determined gravimetrically.

Molecular weights were determined by a Waters Associates High Pressure GPC equipped with four Microstyragel columns (10^5, 10^4, 10^3, and 500 Å) and dual UV and RI detectors. Molecular weights were calculated from a calibration curve obtained with polystyrene standards.

RESULTS AND DISCUSSION

The polymerization of ptBuSt has been investigated by two monomer addition techniques: 1) Adding a quantity of monomer in one rapid dose (conventional technique, control) or 2) introducing a continuous steady stream of monomer to a charge of well-stirred initiating system in a solvent (quasiliving technique).

TABLE 1. Polymerization of p-t-Butylstyrene by the CC/BCl Initiating System with Single Monomer Addition (CH_2Cl_2 solvent, -50°C, $[I]_0 = 1.03 \times 10^{-2}$ mol/dm^3)

Sample	$[M]_0$ (mol/dm^3)	$\overline{M}_n \times 10^{-3}$	$\overline{DP}_n$	$\overline{M}_w/\overline{M}_n$
I 11	1.500	6.33	39.5	6.53
I 12	1.000	6.16	38.5	5.03
I 13	0.710	6.00	37.4	4.32
I 14	0.600	6.85	42.8	3.61
I 15	0.400	5.50	34.3	2.93
I 16	0.200	2.36	14.7	2.95
I 17	0.110	1.65	10.3	1.81
I 18	0.089	1.40	8.7	1.63
I 19	0.067	0.91	5.7	1.45
I 20	0.045	0.77	4.8	1.34

Polymerization by Single Addition of Monomer

Table 1 shows the results of a series of experiments in which various quantities of ptBuSt were rapidly added to a CC/BCl_3 initiating system stirred in CH_2Cl_2 at -50°C.

Assuming that in this system initiation is instantaneous, termination is absent [7], and chain transfer operates at infinite time (after all monomer has been consumed), the number-average degree of polymerization can be described by

$$\overline{DP}_n = \left(1 + \frac{[M]_0}{[I]_0}\right) \Bigg/ \left(1 + \frac{[M]_0}{[I]_0}\,\frac{k_{tr,M}}{k_p + k_{tr,M}}\right) \qquad (1)$$

where $[I]_0$ and $[M]_0$ are the initial concentrations of the initating cumyl cation and ptBuSt, respectively, and k_p and $k_{tr,M}$ are the rate constants for propagation and chain transfer to monomer, respectively [8]. Rearranging Eq. (1) yields a modified Mayo equation:

$$\left(1 + \frac{[I]_0}{[M]_0}\right)\frac{1}{\overline{DP}_n} = \frac{k_{tr,M}}{k_p + k_{tr,M}} + \frac{[I]_0}{[M]_0} \qquad (2)$$

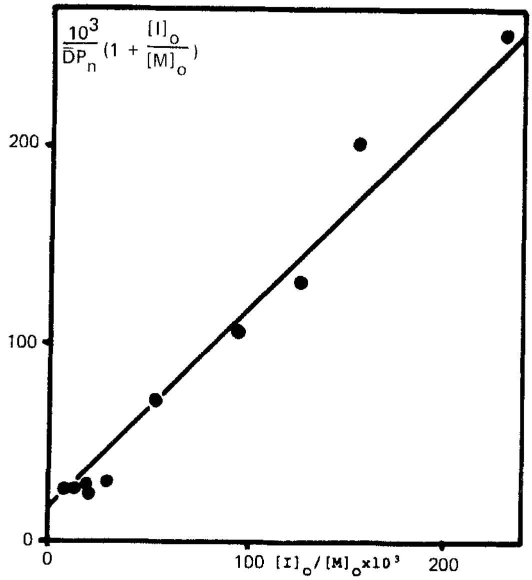


FIG. 1. Modified Mayo plot of the polymerization of p-t-butylstyrene by conventional technique.

Figure 1 shows the modified Mayo plot for the system. The ordinates belonging to high monomer concentrations practically do not differ. However, the plot is linear at $[M]_0 < 0.4$ M, showing that in this range the above assumptions are valid.

Figure 2 is a plot of $\overline{M}_n$ versus $[M]_0$ in the range of $[M]_0 < 0.4$ M. The linearity of the plot and the fact that the line can be smoothly back-extrapolated to the origin is evidence for the existence of quasiliving conditions in this $[M]_0$ range. The numbers in the figure adjacent to the experimental points are molecular weight dispersities ($\overline{M}_w/\overline{M}_n$), and their decreasing tendency with decreasing $[M]_0$ also indicates living character.

Inspection of GPC traces also provides valuable information. As shown by the representative traces in Fig. 3, below ~0.4 M ptBuSt the GPC traces are monomodal and narrow whereas at higher ptBuSt concentrations they are multimodal and broad.

Monomer concentration may affect the nature of the species in the charge. Thus charges were colorless when the [ptBuSt] was higher than ~0.4 M; however, they turned golden-yellow toward the end of the polymerization, i.e., at low [ptBuSt]. In contrast, the charge turned golden-yellow immediately when ptBuSt was added to initiator

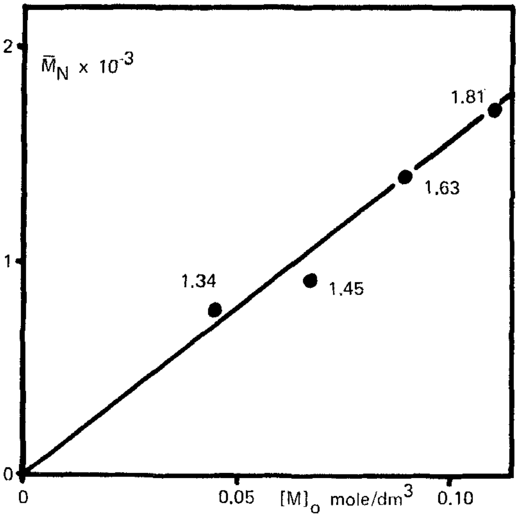


FIG. 2. $\bar{M}_n$ vs $[M]_0$ plots of the polymerization of p-t-butylstyrene by conventional technique at low initial monomer concentrations. $\bar{M}_w/\bar{M}_n$ values are given at each dot.

charges such that the [ptBuSt] in the system was less than ~ 0.4 M. Plesch described a similar color phenomenon in conjunction with the phenylethyl chloride/$AgClO_4$/styrene/CH_2Cl_2 system [9] and attributed it to pseudocationic polymerizations, i.e., to perchlorate ester propagating species that ionize only in the virtual absence of styrene. The system under investigation most likely contains $BCl_4^{\ominus}$ counteranions so that ester formation, i.e., pseudocationic propagation, is unlikely.

In view of these observations the mechanism of the CC/BCl_3/ptBuSt/CH_2Cl_2 polymerization system is a rather conventional one and can be described by Eq. (1) only at relatively low monomer concentrations.

In order to explain the above observations, i.e., the change of color and of the applicability of Eq. (1) with changing monomer concentration, first we assumed that at higher monomer concentrations we are observing an artifact due to the temperature jump caused by the sudden monomer addition to an active initiating charge. However, experiments designed and carried out to test this possibility (see Appendix) convinced us that this is not the case and that the effect is real. While it is difficult to pinpoint the exact nature of the change in the mechanism at ~0.4 M ptBuSt, we speculate that changes in the overall ionicity of the system may be responsible. In general terms the ionicity of the system is affected by the concentration and nature

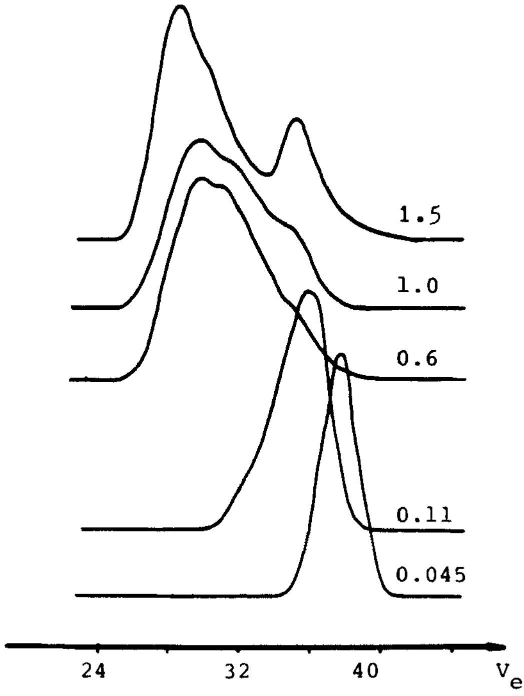


FIG. 3. GPC traces of poly(p-t-butylstyrene) samples prepared by conventional polymerization technique at various initial monomer concentrations (mol/dm^3).

of the solvent. In the case of tight ion pairs the rates of propagation R_p and chain transfer to monomer $R_{tr,M}$ are relatively low and high, respectively. The use of low [M] promotes dissociation of the growing ion pairs and thus increases R_p and decreases $R_{tr,M}$. Further, the use of specific cation- or particularly anion-complexing solvents will promote dissociation and thus quasiliving character. Efforts are being made to develop a semiquantitative theory that explains this effect and other phenomena associated with quasiliving polymerizations.

Polymerization by Continuous Monomer Addition

After having determined that quasiliving polymerization of ptBuSt can be obtained at low monomer concentrations using a conventional technique, efforts have been made to achieve this objective by the

TABLE 2. Polymerization of p-t-Butylstyrene by the CC/BCl_3 Initiating System with Continuous, Steady Monomer Addition (CH_2Cl_2 solvent, -50° C, V_0 = 100 dm^3)

Sample	Monomer consumed At ξ × 10^3 (mol)	$\overline{M}_n \times 10^{-3}$	$\overline{DP}_n$	[P] × 10^3 (mol)	$\overline{M}_w/\overline{M}_n$
A = 2.78 × 10^{-3} mol/min, conversion = 71%, $\overline{DP}_{n,max}$ = 141, ΔT_{stat} = -48.2° C					
I 1	16.90	2.60	16.25	1.04	1.38
I 2	33.80	4.60	28.75	1.18	1.71
I 3	48.60	5.70	35.63	1.36	1.90
I 4	67.60	7.90	49.38	1.37	1.92
I 5	88.60	8.70	54.38	1.63	1.95
I 6	101.30	9.50	59.38	1.71	1.90
A = 5.56 × 10^{-3} mol/min, conversion = 91%, $\overline{DP}_{n,max}$ = 63, ΔT_{stat} = -45.5° C					
H 8	18.20	1.70	10.62	1.71	1.29
H 9	36.40	3.60	22.50	1.62	1.45
H 10	54.60	4.60	28.75	1.90	1.40
H 11	72.80	5.50	34.38	2.12	1.84
H 13	90.90	5.90	36.88	2.47	2.12
H 14	109.10	6.40	40.00	2.73	1.97
A = 11.12 × 10^{-3} mol/min, conversion = 77%, $\overline{DP}_{n,max}$ = ∞, ΔT_{stat} = -42.3° C					
D 1	21.40	3.03	18.90	1.13	2.7
D 2	42.80	6.82	42.62	1.00	2.3
D 3	64.20	10.17	63.56	1.01	2.6
D 4	85.60	13.42	83.92	1.02	2.1
D 5	107.00	16.95	105.95	1.01	2.1
A = 19.98 × 10^{-3} mol/min, conversion = 71%, $\overline{DP}_{n,max}$ = ∞ ΔT_{stat} = -37.7° C					
H 3	14.20	1.73	11.54	1.23	1.7
H 4	28.40	3.70	24.27	1.17	2.1
H 5	42.60	5.83	37.37	1.14	2.1
H 6	56.80	8.03	50.27	1.13	2.1
H 7	71.00	9.60	98.70	1.15	2.1

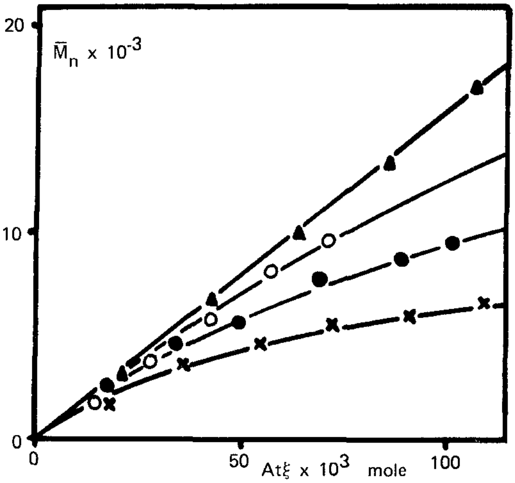


FIG. 4. $\overline{M}_n$ vs consumed monomer plots of the polymerization of p-t-butylstyrene by continuous steady monomer addition technique: (●) I 1-6, (x) H 8-14, (▲) D 1-5, (○) H 3-7.

continuous, slow monomer addition technique described by Faust et al. [1]. The experimental results are collected in Table 2. The M_n vs consumed monomer plot is shown in Fig. 4.

Again, it is assumed that in the system under investigation initiation is instantaneous ($[I]_0 = [M^{\oplus}]$), termination is reversible, and transfer to monomer is operational. Thus

$$\overline{DP}_n = \frac{\int_0^t k_p[M][I]_0\,dt}{[I]_0 + \int_0^t k_{tr,M}[M][I]_0\,dt} \tag{3}$$

Since

$$\int_0^t k_p[M][I]_0\,dt = At\xi \tag{4}$$

by combining (4) and (5), one obtains

$$\overline{DP}_n = \frac{At\xi}{[I]_0 + (k_{tr,M}/k_p)At\xi} \tag{5}$$

From (6),

$$[P] = \frac{At\xi}{\overline{DP}_n} = [I]_0 + \frac{1}{\overline{DP}_{n,max}} At\xi \qquad (6)$$

where $\overline{DP}_{n,max} = k_p/k_{tr,M}$ and $[P]$ = concentration of polymer molecules formed during time t.

Equation (6) is the diagnostic expression described in Ref. 10 (see Fig. 2 in Ref. 10) used to classify the various living systems. Figure 5 shows this representation for four series of experiments (see also Table 2). For convenience, the values are given in moles.

It is gratifying that the intercepts of all four plots extrapolate to $[I]_0 \approx 1.0 \times 10^{-3}$ mol which is within what is considered to be experimental error of the amount of CC initiator used. The slopes of the lines give $\overline{DP}_{n,max}$ (shown in Table 2). Significantly, the horizontal slope in the experimental Series D 1-5 and H 3-7 indicate that in these runs during the investigated short time period, the number of active centers did not change. The slopes of the plots associated with Series I

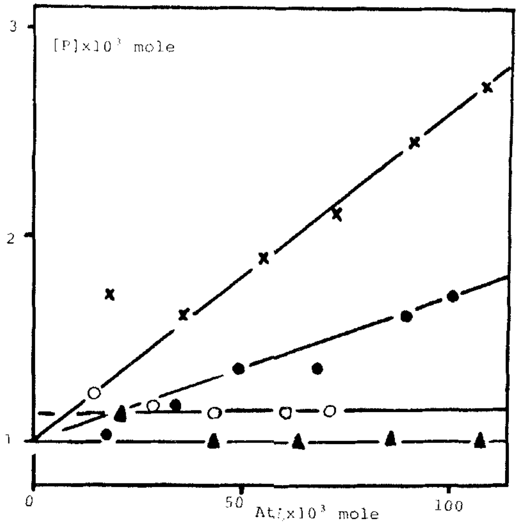
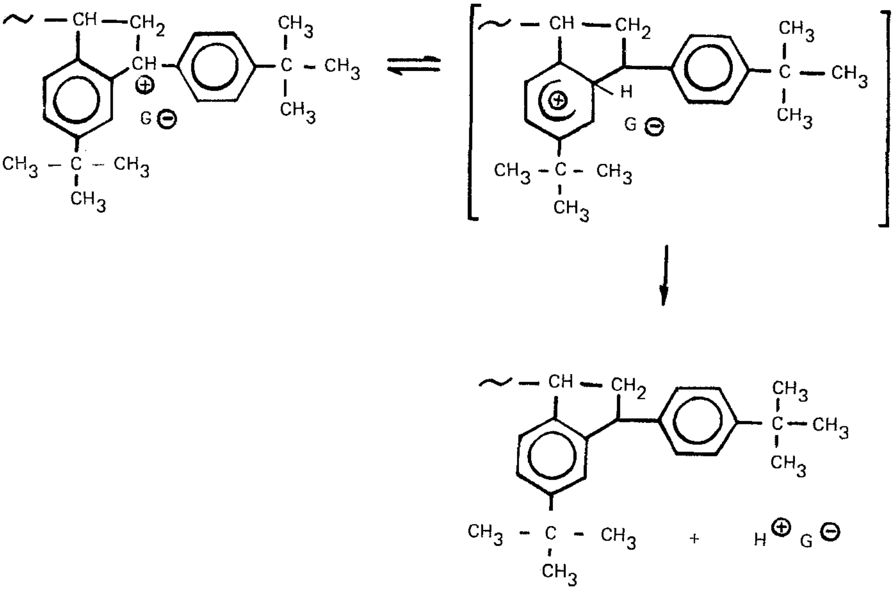


FIG. 5. Number of polymer molecules ([P]) vs monomer consumed (Atξ) plot of the polymerization of p-t-butylstyrene by continuous steady monomer addition technique. (For notations, see Fig. 4).

1-6 and H 8-14 gave finite $\overline{DP}_{n,max}$ values, indicating the presence of chain transfer to monomer, i.e., according to the classification developed for quasiliving polymerizations, these systems are QL_{R1}.

It is of interest to speculate on the processes that lead to the results compiled in Table 2. Decreasing the monomer addition rate from 19.98 (H 3-7) to 5.56 × 10^{-3} mol/min (H 8-14) increased the conversions from 71 to 91%; however, a further decrease in the addition rate to 2.78 × 10^{-3} mol/min (I 1-6) led to a drop in conversions to 71%, i.e., to the accumulation of unconverted monomer. The decreasing of conversions may be explained by assuming that the number of active propagating centers decreases due to chain transfer by intramolecular alkylation leading to the formation of an indane skeleton:



The transition state is visualized to be rather stable [1] and the rate-determining step to be proton expulsion. The subsequent event, i.e., protonation of monomer, is most likely rapid, thus the rate of intramolecular alkylation (indane formation) is independent of monomer concentration. In contrast, the rate of propagation is affected by monomer concentration so that a decrease in [M] would increase indane formation. The extended lifetime of the transition state leading to indane formation would further decrease the rate of propagation and thus would lead to the decrease of conversion. Absence of indane formation at higher monomer concentrations may be due to increased rate of propagation.

TABLE 3. Polymerization of p-t-Butylstyrene by the CC/BCl_3 Initiating System with Repeated Monomer Addition (CH_2Cl_2 solvent, -50°C)

Sample	Monomer consumed × 10^3 (mol)	$\overline{M}_n \times 10^{-3}$	$\overline{DP}_n$	[P] × 10^3 (mol)	$\overline{M}_w/\overline{M}_n$
K 13	10.0	1.3	8.13	1.23	1.27
K 14	20.0	2.3	14.38	1.39	1.39
K 15	30.0	3.2	20.00	1.50	1.94
K 16	40.0	3.7	23.13	1.73	2.12

These results and a body of other evidence [1-5] indicate that quasiliving polymerizations can only be attained at specific monomer addition rates. In the case of styrene derivatives where indane formation may occur, quasiliving polymerizations will occur neither at too low monomer input rates because of intramolecular alkylation nor at too high input rates because of monomer accumulation and consequent chain transfer to monomer. In the present instance the monomer input rates A = 2.78 and 5.56 mmol/min in Series H 8-14 and I 1-6 were too low and indane formation depressed $\overline{DP}_{n,max}$. (GPC traces of samples withdrawn during Series I 1-6 showed 100% conversion at the beginning of the run and monomer accumulation as the experiment progressed.) In Series H 3-7 and D 1-5 the input rates were higher (A = 11.12 and 19.98 mmol/min) and the systems approached quasiliving conditions. Interestingly, in Series H 3-7, where the input rate was the highest, monomer accumulation has occurred (conversion is 71%), nonetheless favorable conditions prevailed because the residual [ptBuSt] was still only 0.3 M, i.e., still in the concentration range found to be optimal by conventional polymerizations.

Finally, a series of experiments have been carried out by intermittent monomer addition. In these experiments we added a quantity of monomer (0.1 M ptBuSt) in one rapid dose to the initiator charge as described in the previous section. After 10 min of stirring a sample was withdrawn and another aliquot of 0.1 M monomer was introduced. This procedure was repeated four times (four doses of monomer, four samples). The data are compiled in Table 3, and Fig. 6 is a plot of $\overline{M}_n$ versus cumulative amount of monomer added. $\overline{DP}_n$ increases with monomer input; however, the plot is not linear which indicates the presence of chain transfer to monomer. Figure 7 is a plot of [P] versus cumulative amount of monomer consumed. Again, the plot is a straight line (QL_{R1} system), the intercept of which

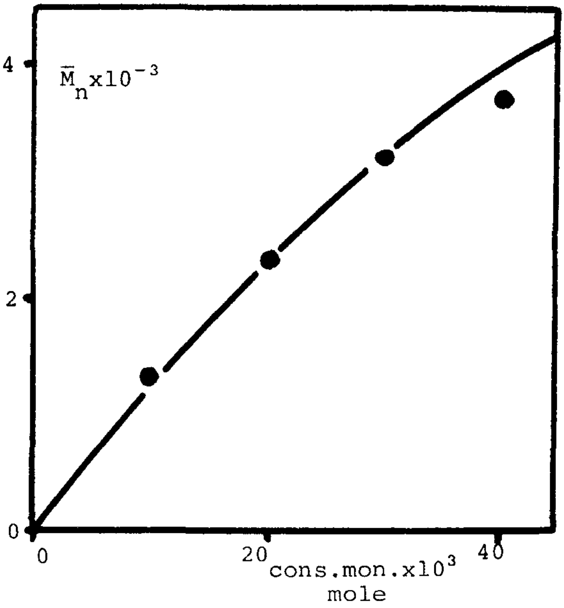


FIG. 6. $\bar{M}_n$ vs monomer consumed plot of the polymerization of p-t-butylstyrene by repeated monomer addition.

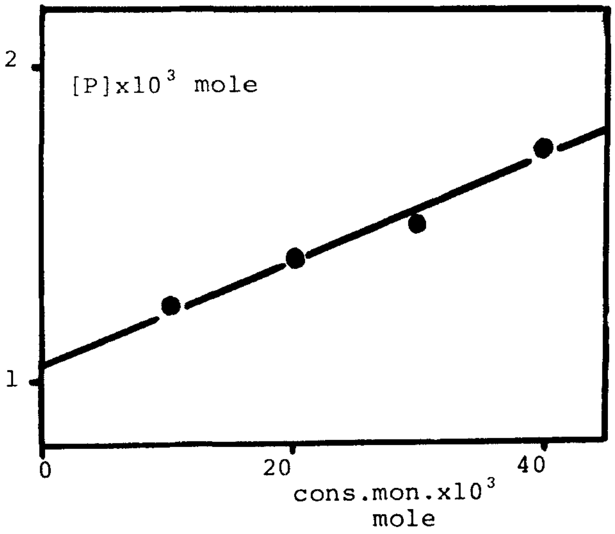


FIG. 7. Number of polymer molecules ([P]) vs monomer consumed plot of the polymerization of p-t-butylstyrene by repeated monomer addition.

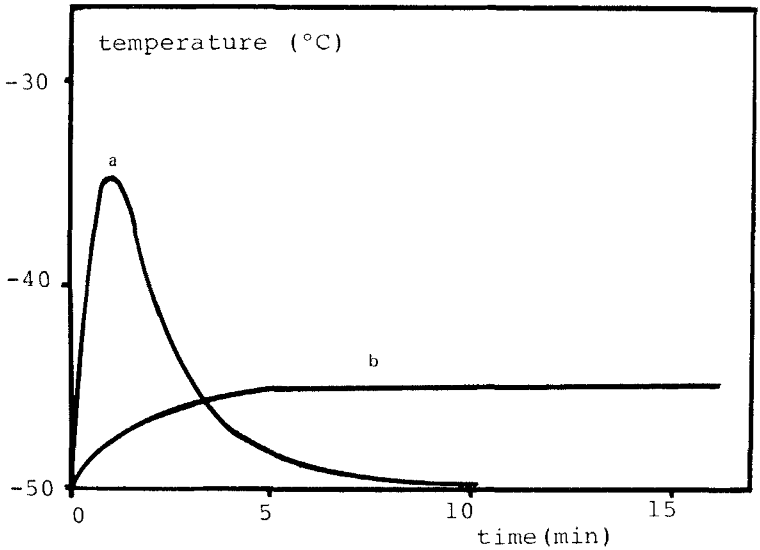


FIG. 8. Change of temperature during the polymerization of p-t-butylstyrene by conventional technique (Curve a, 0.1 mol monomer in one dose), and by quasiliving technique (Curve b, 5.6 × 10^{-3} mol/min monomer addition rate).

gives $[I]_0 = 1.03 \times 10^{-3}$ mol, close to the theoretical value; the slope corresponds to $\overline{DP}_{n,max} = 59$. It is of interest that this $\overline{DP}_{n,max}$ is still higher than that obtained by a single monomer addition at high monomer concentration (i.e., $\overline{DP}_n = 42$ at [ptBuSt] = 1.5 M; see Table 1).

APPENDIX: THE EFFECT OF HEAT EVOLUTION DURING MONOMER ADDITION ON MOLECULAR WEIGHTS

The addition of a quantity of monomer to a stirred cooled charge of active initiating system results in immediate polymerization accompanied by heat evolution. The amount of heat generated over a given period of time, ΔH_p, is a function of the amount of monomer introduced. The temperature increase depends on ΔH_p, on the heat capacity of the system C_p, and on the heat transfer coefficient a. Figure 8 shows the temperature profiles determined experimentally: Curve a, adding 0.1 mol monomer to 100 mL charge in one dose

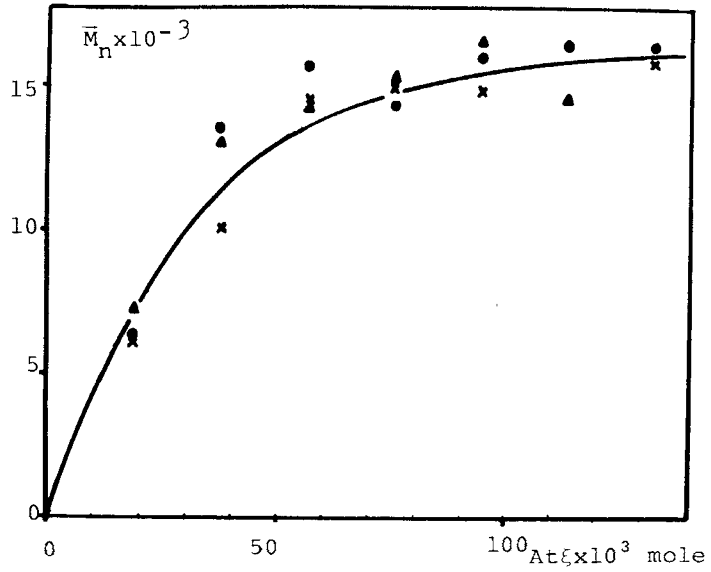


FIG. 9. $\overline{M}_n$ vs monomer consumed plot of the polymerization of p-t-butylstyrene by continuous steady monomer addition at -30°C (×), -50°C (●), and -70°C (▲).

(conventional technique, $[M]_0 = 1.0$ M); Curve b, applying continuous monomer addition (quasiliving technique) with $A = 5.6 \times 10^{-3}$ mol/min. The initial charges were 1.03×10^{-3} mol CC and 3.5×10^{-3} mol BCl_3 in 100 mL CH_2Cl_2 at -50°C.

The temperature jump by the conventional technique was 14.5°C. It is noteworthy that the extent of the temperature effect was the same, independent of the reagent introduction sequence, i.e., by using 1) CH_2Cl_2, 2) CC, 3) ptBuSt, 4) BCl_3 solution or 1) CH_2Cl_2, 2) BCl_3, 3) CC, 4) monomer solution.

Temperature profiles prevailing in continuous runs were determined at -30, -50, and -70°C (a representative profile at -50°C is shown in Fig. 8, Curve b). Figure 9 shows $\overline{M}_n$'s as a function of monomer consumed at these temperatures. The fact that the $\overline{M}_n$'s are independent of temperature indicates that $k_p/k_{tr,M}$ is also independent of temperature in this range.

Obviously, temperature control is much better by continuous, slow monomer addition than by single or sequential monomer addition. The temperature difference between the charge and the cooling bath with continuous monomer addition is

$$\Delta T(t) = \frac{-\Delta H_p}{C_p}\frac{A\xi}{a}(1 - e^{at})$$

where ΔH_p is the reaction enthalpy, C_p is the heat capacity of the system, A is the monomer input rate, ξ is the conversion, and a is the heat transfer coefficient. After a sufficient time $\Delta T(t)$ will be equal to the stationary temperature difference ΔT_{stat}:

$$\Delta T_{stat} = \frac{-\Delta H_p}{C_p}\frac{A\xi}{a}$$

According to pertinent references, ΔH_p^{ss} for styrene polymerization is -66.5 kJ/mol [12], and C_p is 122 J/K for 100 cm^3 CH_2Cl_2 at -50°C [12]. By determining ΔT_{stat} during a polymerization, one can obtain a. Thus we found a = 0.633 min^{-1}. By knowing this value and using ΔH_p^{ss} for styrene, one can approximate ΔT_{stat} in our experiments. Table 2 lists ΔT_{stat} values calculated to prevail in our continuous monomer addition experiments. Since all these values are in the -38 to -48°C range, i.e., in a temperature range over which k_p/k_{tr} is independent of temperature (see Fig. 9), the observed sudden change in the polymerization mechanism is most likely not due to insufficiency of temperature control. This conclusion is further substantiated by the fact that quasiliving polymerization has been demonstrated to occur in experiments in which the temperature effect was the largest (i.e., Experiments D 1-5 and H 3-7 with ΔT_{stat} = 7.7 and 12°C, respectively).

ACKNOWLEDGMENTS

Financial contributions by the NSF (INT-78-27245) and the Hungarian Academy of Sciences are gratefully acknowledged.

REFERENCES

[1] R. Faust, A. Fehérvári, and J. P. Kennedy, J. Macromol. Sci. Chem., A18(9), 1209 (1982).

[2] J. Puskás, G. Kaszás, J. P. Kennedy, T. Kelen, and F. Tüdős, Ibid., A18(9), 1229 (1982).

[3] J. Puskás, G. Kaszás, J. P. Kennedy, T. Kelen, and F. Tüdős, Ibid., A18(8), 1315 (1982).
[4] M. Sawamoto and J. P. Kennedy, Ibid., A18(8), 1245 (1982).
[5] M. Sawamoto and J. P. Kennedy, Ibid., A18(8), 1293 (1982).
[6] J. P. Kennedy and R. A. Smith, J. Polym. Sci., Polym. Chem. Ed., 18, 1523 (1980).
[7] J. P. Kennedy, S. Y. Huang, and S. C. Feinberg, Ibid., 15, 2869 (1977).
[8] L. H. Peebles, Molecular Weight Distribution in Polymers, Wiley-Interscience, New York 1971, Eq. (15) on p. 173.
[9] A. Gandini and P. H. Plesch, J. Polym. Sci., Part B, 3, 127 (1965).
[10] J. P. Kennedy, T. Kelen, and F. Tüdős, J. Macromol. Sci.–Chem., A18(8), 1189 (1982).
[11] S. C. Guhaniyogi and J. P. Kennedy, Polym. Bull., 4, 267-274 (1981).
[12] J. Brandrup and E. H. Immergut (eds.), Polymer Handbook, 2nd ed., Wiley, New York, 1975.