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Controlled Radical Polymerization by Degenerative Transfer: Effect of the Structure of the Transfer Agent

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ABSTRACT: Control of the radical polymerization of styrene and acrylates has been achieved by using alkyl iodides in a degenerative transfer process. Various transfer agents of the type R–I were explored. Of those examined, 1-phenylethyl iodide, iodoacetonitrile, and iodoform were found to be effective in controlling molecular weights and for providing polymers with relatively low polydispersities, $M_w/M_n \leq 1.5$. Relatively good control has been also achieved with perfluoroalkyl iodides, whereas most alkyl and aryl iodides have been ineffective transfer agents. Also explored were the effects of initiator structure and reaction temperature on the polymerization systems.

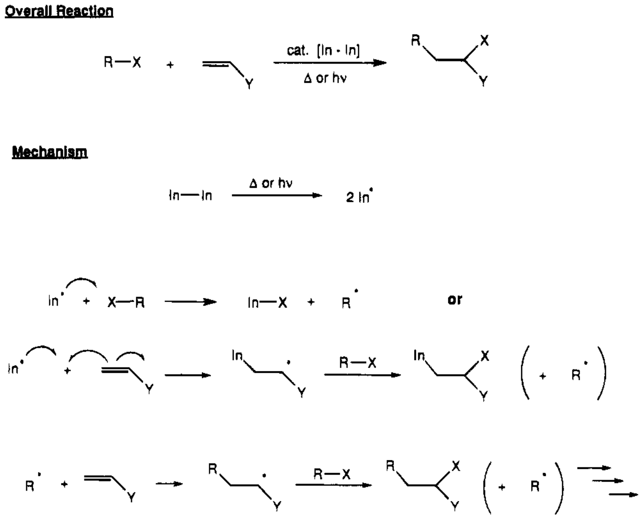
Introduction

The design and synthesis of new polymers is desirable to obtain materials with novel physical properties. This can be achieved by development of new monomers for polymerization or by using old monomers for new polymers with novel architectures, resulting in new physical properties. Most notably, these architectures include block copolymers and star polymers. With the large number of low-cost monomers currently available, the most effective methodology of developing polymers with new physical properties appears to be the synthesis of polymers with new topologies. These new architectures require that either separate polymers be formed with functional end groups and then joined together or the successive addition of a second monomer after the complete, or nearly complete, conversion of a first monomer.

The step-growth (condensation) polymerizations are based on the reaction of polymers with functional end groups. However, vinyl monomers, most of which are capable of being polymerized by radical means, require the use of transfer agents and/or functionalized initiators and terminators capable of imparting functional groups at the polymer chain ends to form telechelic polymers. These functionalized polymers can then be reacted with a second group of polymers which contain functional groups which are capable of reacting with the first set. An example would be a group of polymers with carboxylic acid end groups and another with amine end groups. These polymers, however, are generally of very low molecular weight and usually have broad polydispersities, $M_w/M_n \sim 2$.

Living polymerizations, that is, polymerizations without transfer and termination, allow for the synthesis of block copolymers in a single one-pot synthesis by the simple addition of a second monomer at the complete consumption of the first monomer. As the process of adding successive monomers can be repeated, it is possible to synthesize polymers containing numerous blocks of different segments. These polymerizations usually proceed by either anionic or cationic mechanisms. However, the number of polymers which are capable of being polymerized by ionic means is limited. Because of the larger number of monomers capable of undergoing radical polymerization, it is desirable to find new methods for radical polymerization which are living in nature, i.e., without transfer and termination. These living systems have the characteristics of linear molecular weight growth with conversion and narrow molecular weight distributions, M_w/M_n.

Scheme 1



Recently, three processes to obtain “living” radical polymerizations have been reviewed.[1] One of these methods, degenerative transfer, has been used to obtain the controlled polymerization of styrene and acrylates and is the subject of this paper.

Atom/group transfer additions and cyclizations have been used successfully in organic reactions.[2,3] In these organic systems (Scheme 1), the radical, R•, is generated from the transfer agent R–X by abstraction of the atom or group, X. This is first accomplished by the abstraction of X from R–X by an initiator radical, In•. The initiator radical, In•, is generated by decomposition of a conventional initiator, i.e., AIBN or BPO, by either heating or irradiating the reaction mixture. The radical R• can then react with an alkene to form the radical species, $R{-}CH_2CHY^\bullet$. This species can subsequently abstract the group X from R–X, to form the dormant species, $R{-}CH_2CHY{-}X$, and R•. The process can then repeat itself. Because this process is a chain reaction, only small quantities of the initiator, relative to the transfer agent, are required to drive the reaction to completion.

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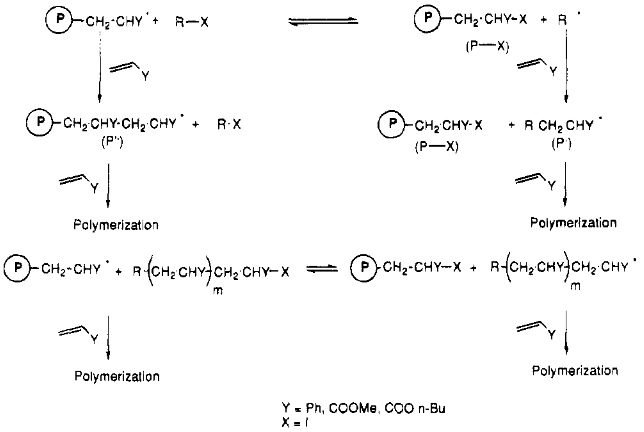
Scheme 2



In these systems, the species, R•, and R–CH_2CHY•, are chosen so as to prevent subsequent abstraction of X from R–CH_2CHY–X. However, if the reactivities of R–X and R–CH_2CHY–X are similar, competitive atom/group transfer may occur, leading to the formation of polymers, i.e., degenerative transfer. Iodine and the phenylselenyl group have been successfully used as the X group in simple organic systems.[2,3]

A similar approach has been previously reported for perfluorinated alkyl iodides[4] and for styrene derivatives.[5] In this paper, we report more detailed information on the structural requirements for the success of the transfer agents, R–X, in controlling the free-radical polymerization.

Although it is impossible to eliminate termination in radical polymerizations, the contribution of termination can be significantly lowered under appropriate conditions.[1] In degenerative transfer (Scheme 2), a transfer agent, R–X, reacts with a propagating radical to form the dormant polymer chain P–X. The new radical, R•, can then reinitiate polymerization. Because of this, the concentration of the polymer chains is equal to the sum of the concentrations of the transfer agent and consumed initiator. The newly formed polymer chain, P'•, can then propagate or react with the dormant polymer chain P–X or R–X. This is significantly different from degradative transfer, used in typical telomerization reactions, in which the dormant polymer chains, P–X, can not be reactivated after initial reaction with the transfer agent.[6]

In the systems to be described, it should be noted that termination does occur. The polymerization systems described here have been designed so that the proportion of irreversibly terminated chains is kept at low levels, not exceeding 10–30% of the total number of polymer chains. The systems based upon degenerative transfer are not living in the purist sense. However, they do allow for the preparation of polymers with controlled molecular weights and polydispersities much lower than those found in conventional free-radical polymerizations. Moreover, they allow for the control of terminal functionalization, which is important in the synthesis of telechelic materials.

Results and Discussion

1-Phenylethyl Iodide. The process of degenerative transfer implies that the transfer reaction should, ideally, be thermodynamically neutral. That is, the transfer of the iodine atom between the dormant polymer chain and the propagating polymer chain should involve neither a loss nor a gain in free energy. However, any propagating chain must first abstract the iodine atom from the initial transfer agent, R–X. It is here where the effect of the structure of the transfer agent is most important. An ideal candidate for a thermodynamically neutral transfer would be one that resembles the propagating chain end. For the polymerization of styrene this would be 1-phenylethyl derivatives. In terms of kinetics, the rate constant of exchange between the dormant and active species should be equal to or greater than the rate constant of propagation.

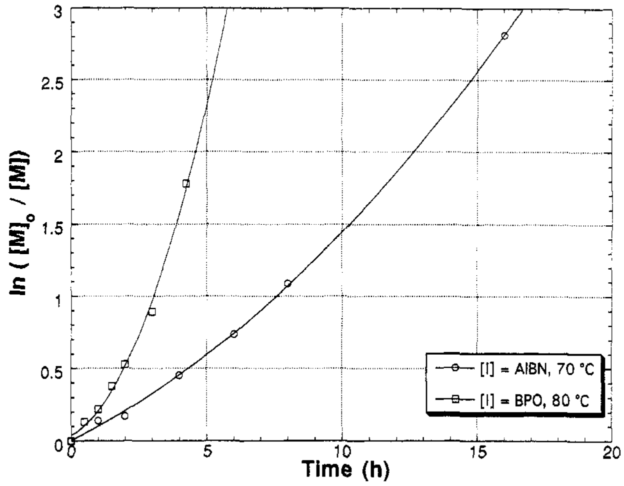


Figure 1. Kinetics of the bulk polymerization of styrene. $[1\text{-PEI}]_0 = 0.1$ M, $[I]_0 = 0.03$ M.

The polymerization was initially carried out in bulk at 70 °C using AIBN as the initiator. The transfer agent which was used was 1-phenylethyl iodide, 1-PEI. The slight increases in the rate of polymerization in semilogarithmic plots (Figure 1) at higher conversions might be due to an increase in the viscosity of the reaction medium. The result of this increase in viscosity is a lowering of the rate of termination, due to restricted mobility of the polymer chain ends, while at the same time, the rate of propagation remains nearly constant, as monomer can more easily diffuse to the active chain end than can another active chain end. This occurs only at higher conversions, however, and the increase in reaction rate is observed at higher conversions (Figure 1).

More importantly, the molecular weight of the polymer increased with conversion and approached the theoretical molecular weight at 100%, as defined by DP = $\Delta[M]/([R-I]_0 + \Delta[I])$ (Figure 2). The theoretical M_n was determined by estimation of the consumption of the initiator at the end of the reaction. This was not the case when the polymerizations were performed in the absence of the transfer agent. As can be seen from Figure 2, the molecular weight of the resulting polymers in the presence of 1-phenylethyl iodide was approximately 8000, while the molecular weight of the polymers obtained without the transfer agent was around 40 000.

The consumed initiator is considered to account for termination of the propagating radicals. The radicals generated by the initiator must terminate irreversibly, i. e., by combination or disproportionation, for if they did not, the rate of the polymerization would dramatically increase as the reaction progressed. Figure 3 shows typical GPC traces of polymer samples taken at various intervals.

Also significant was that the polydispersities of the polymer samples were essentially the same at high conversions as they were at lower conversions, M_w/M_n ~ 1.4 (Figure 4).

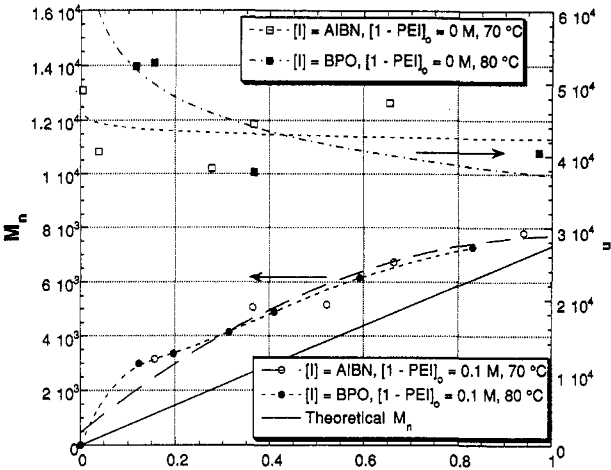


Figure 2. Dependence of M_n upon conversion for the bulk polymerization of styrene. $[I]_0 = 0.03$ M.

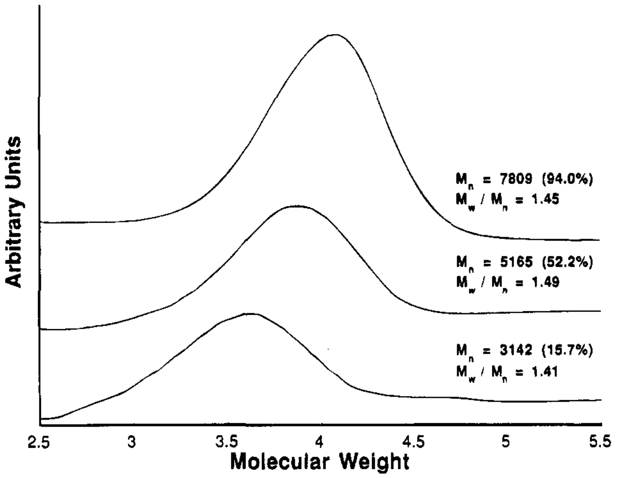


Figure 3. Typical GPC traces from the bulk polymerization of styrene at 70 °C. $[1-PEI]_0 = 0.1$ M, $[AIBN]_0 = 0.03$ M.

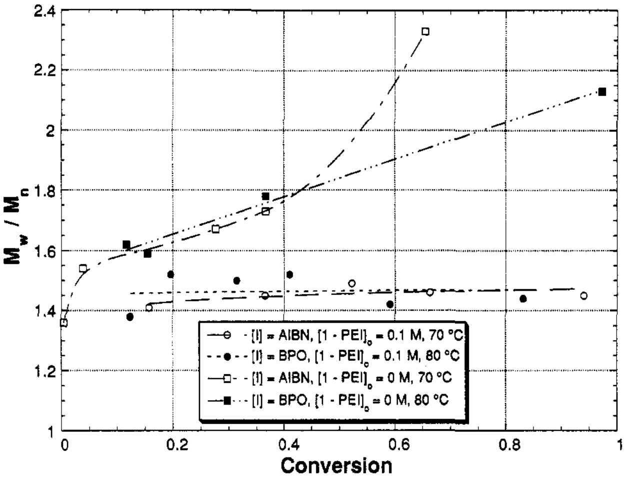


Figure 4. Dependence of M_w/M_n upon conversion for the bulk polymerization of styrene. $[I]_0 = 0.03$ M.

When the polymerization was carried out with no transfer agent, the molecular weight distributions were considerably broader, $M_w/M_n > 2$. The molecular weight increase with conversion and the low polydispersities prove that the degenerative transfer process does allow for control of the radical polymerization even with a small percentage of irreversibly terminated polymer chains.

As can be seen from Figures 2 and 4, in terms of molecular weight growth and polydispersities, there was essentially no difference in the use of BPO as an initiator in comparison to AIBN when 1-phenylethyl iodide was used as a degenerative transfer agent. However, the rate of polymerization was faster due to the polymerization being carried out at a higher temperature, (Figure 1).

Temperature. The effect of temperature upon the polymerization of styrene was investigated using 1-phenylethyl iodide as the transfer agent at 50, 70, and 90 °C. From Table 1, it can be seen that temperature did affect the rate of polymerization, as expected. At 70 °C, the reaction required 16.0 h to reach 94% conversion, while at 50 °C, 39.0 h was required. However, when the polymerization was carried out at 90 °C, a limiting value of about 50% conversion was obtained due to complete consumption of the AIBN. In all three cases, the polymer's molecular weight increased with conversion (Figure 5). From the fact that the molecular weight dependence upon conversion was the same for all three temperatures, it can be concluded that the relative rate of exchange and that of propagation were similar in the temperature range of 50−90 °C. This will be discussed in more detail in a forthcoming paper.[7]

Effect of R−X as the Transfer Agent. In order to determine what effect, if any, the structure of R−X had upon the control of the polymerization, various alkyl iodides were used as transfer agents in the polymerization of styrene. Table 1 lists the compounds which were used along with conversion and molecular weight data.

The first compounds used were the iodomethanes (Figure 6). When iodomethane and diiodomethane were used as transfer agents, polymers with higher than expected molecular weights were obtained. Both had relatively large polydispersities, $M_w/M_n \sim 2$. The use of iodoform led to molecular weight growth with conversion, final $M_n \sim 5000$ at 80% conversion. Also the polymers had narrower molecular weight distributions, $M_w/M_n \sim 1.4$. In this case, the rate of transfer could be comparable to that of propagation.

Alkyl iodides were used to explore the effect of iodine substitution at primary, secondary, and tertiary R groups (Figure 7). Polymers obtained when *n*-propyl iodide, isopropyl iodide, and *tert*-butyl iodide were used all had molecular weights higher than predicted by $\Delta[M]/[R-I]_0$ and had relatively broad polydispersities, $M_w/M_n \sim 2$.

Perfluoroalkyl compounds were studied next. The two perfluoroalkyl iodide compounds, perfluorohexyl iodide and perfluoroisopropyl iodide, were used as transfer agents with some success. The molecular weights of the polymers obtained when these two transfer agents were used were, however, higher than predicted but had relatively narrow molecular weight distributions, (Figure 8). The molecular weight dependence upon conversion did not approach the theoretical values to the same extent as when 1-phenylethyl iodide was used, as shown in Figure 8. The molecular weights of the polymers were around 11 000, when theoretically the M_n should have been $M_n \sim 7000$.

The aryl derivatives, iodobenzene and 1,4-diiodobenzene, were employed with no success in controlling molecular weight growth with conversion (Figure 9). The polymers also had relatively broad molecular weight distributions, $M_w/M_n \sim 2$.

In addition, iodoacetonitrile was used as the transfer agent. Figure 10 shows the molecular weight growth of the polymer chains with conversion. The polydispersity of the final sample was $M_w/M_n = 1.41$.

Table 1. Use of Various Alkyl Iodides in the Bulk Polymerization of Styrene[a]

R–I	initiator	time (h)	conv (%)	M_n theory/found	M_w/M_n
none	AIBN	6.0	86	65500	3.7
	BPO	3.5	97	40480	2.1
1–PEI	AIBN	16.0	94	6580/7810	1.5
	AIBN[b]	39.0	92	6500/7830	1.4
	AIBN[c]	2.0	52	3670/5840	1.5
	BPO	4.25	83	6570/7280	1.4
iodomethane	BPO	3.0	93	7380/34500	2.1
diiodomethane	BPO	5.5	91	7250/20140	2.0
iodoform	BPO	5.5	80	6360/5120	1.4
carbon tetraiodide	BPO	5.5	31	2480/390	1.0
n–propyl iodide	BPO	3.0	99	7420/34050	2.2
isopropyl iodide	BPO	3.0	86	6460/33730	2.0
tert-butyl iodide	BPO	4.83	57	4300/25540	2.0
perflouroisopropyl iodide	BPO	4.5	94	7490/10570	1.5
perflourohexyl iodide	BPO	4.5	94	7440/11200	1.5
iodobenzene	BPO	4.0	98	8260/29730	2.0
1,4–diiodobenzene	BPO	4.25	77	6050/33620	2.0
1,4–bis(2-iodoethyl)benzene	BPO	4.0	74	5850/20800	2.8
iodoacetonitrile	BPO	4.5	83	6550/5800	1.4

[a] For all polymerizations $[R-I]_0 = 0.1$ M, $[\text{initator}]_0 = 0.03$ M. Temperature: BPO, 80 °C; AIBN, 70 °C, except. [b] 50 °C. [c] 90 °C.

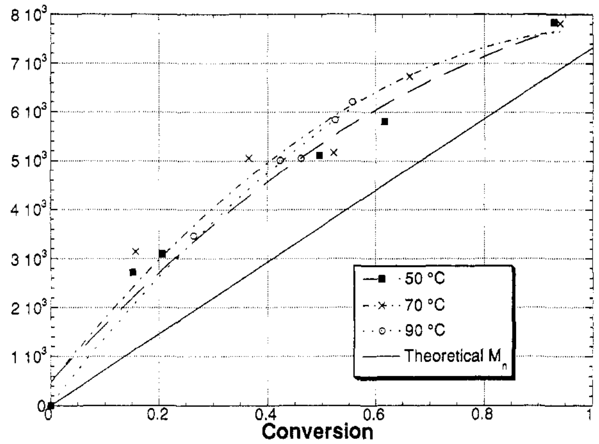


Figure 5. Dependence of M_n upon conversion for the bulk polymerization of styrene at various temperatures. $[1-PEI]_0 = 0.1$ M, $[AIBN]_0 = 0.03$ M.

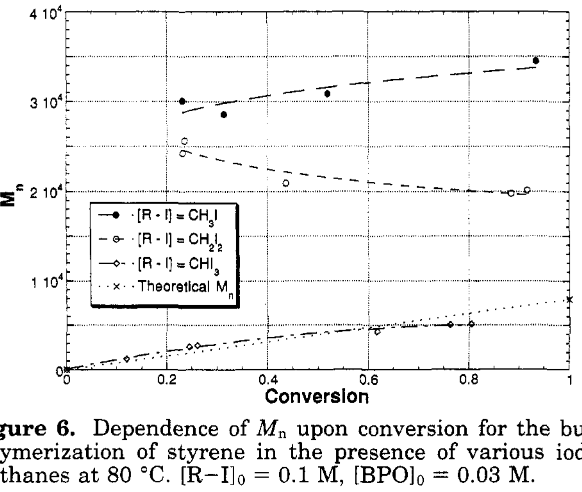


Figure 6. Dependence of M_n upon conversion for the bulk polymerization of styrene in the presence of various iodomethanes at 80 °C. $[R-I]_0 = 0.1$ M, $[BPO]_0 = 0.03$ M.

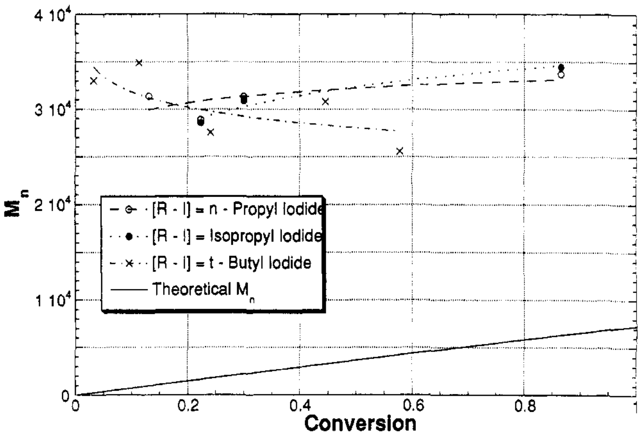


Figure 7. Dependence of M_n upon conversion for the bulk polymerization of styrene in the presence of various alkyl iodides at 80 °C. $[R-I]_0 = 0.1$ M, $[BPO]_0 = 0.03$ M.

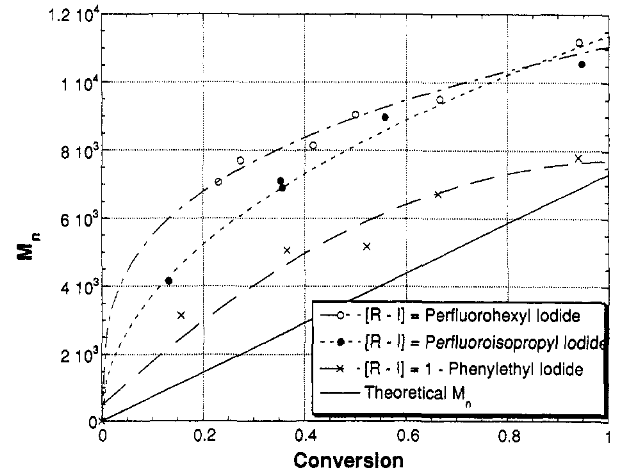


Figure 8. Dependence of M_n upon conversion for the bulk polymerization of styrene in the presence of perfluoroalkyl iodides at 80 °C. $[R-I]_0 = 0.1$ M, $[BPO]_0 = 0.03$ M.

From the above experiments, the following conclusions can be made about the requirements for R–X to be a successful degenerative transfer agent. First the carbon–iodine bond must be sufficiently labile. This is to allow for facile transfer of the iodine atom from the transfer agent to the propagating radical. In terms of kinetics, this translates into a rate of degenerative transfer comparable to the rate of propagation. Secondly, the R groups which were successful had functional groups which were able to stabilize the resulting radical, through either inductive or resonance effects.

The inductive/polar effects must be strong enough to stabilize the newly formed radical. This was shown in the case of the polyiodomethanes. When iodomethane or diiodomethane was used as the transfer agent, there was no control of the polymerization. However, when iodoform was used, there was control of the polymerization. Presumably, at least two additional iodine

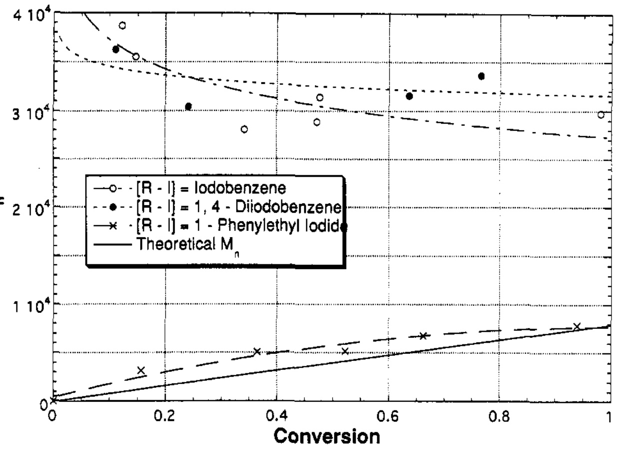


Figure 9. Dependence of M_n upon conversion for the bulk polymerization of styrene in the presence of various phenyl iodides at 80 °C. $[R-I]_0 = 0.1$ M, $[BPO]_0 = 0.03$ M.

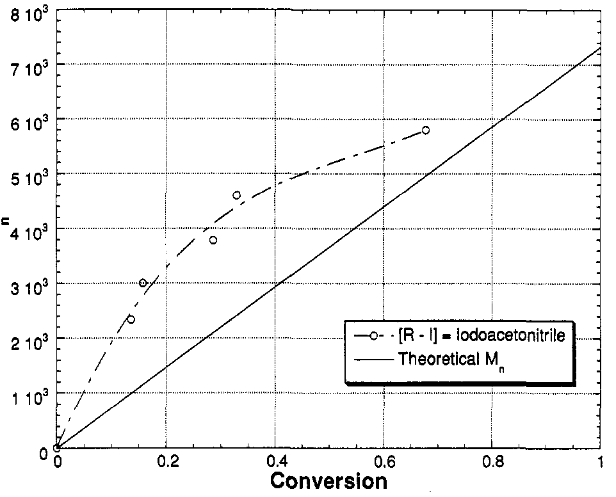


Figure 10. Dependence of M_n upon conversion for the bulk polymerization of styrene in the presence of iodoacetonitrile at 80 °C. $[ICH_2CN]_0 = 0.1$ M, $[BPO]_0 = 0.03$ M.

atoms were required to lower the E_a for transfer to allow for the rate of transfer to be comparable to the rate of propagation. Similar effects are responsible for the successful use of perfluoroalkyl iodides.

The stabilization of the radical by resonance effects has some qualifiers. Although the radicals generated by abstraction of the iodine atom from the iodobenzenes might be stabilized by delocalization around the aromatic ring, there is no control of the polymerization, indicating that the rate of transfer is much lower than that of propagation. This is due to the aryl–iodine bond being too strong. However, 1-phenylethyl iodide, upon abstraction of the iodine atom, forms a radical which is delocalized over the α-carbon atom and the benzene ring. The 1-phenylethyl iodide compound is a successful transfer agent. Apparently, the increased delocalization of the 1-phenylethyl group allows for easier abstraction of the iodine atom as compared to the iodobenzenes. The same is true for the cyano group in iodoacetonitrile.

Other halogens, such as bromine and chlorine, were tried but were not successful in controlling the polymerization of styrene. Again, this is presumably due to the increased strength of the carbon–halogen bond. Apparently, the carbon–iodine bond is the only one which is sufficiently labile to allow for a fast rate of degenerative transfer at temperatures below 100 °C.

Monomers. Table 2 shows the results of the polymerization of various monomers with AIBN as the initiator and 1-phenylethyl iodide as the transfer agent. The first monomer is styrene, which has already been discussed. The next monomers to be studied were acrylates, specifically methyl acrylate and butyl acrylate. Figures 11 and 12 show for methyl acrylate and butyl acrylate, respectively, the molecular weight dependence upon conversion for the polymer systems and also the resulting polydispersities of the polymer samples.

As can be seen from the two figures, the molecular weights of the polymer grew with conversion and approached the theoretical values, but the polydispersities were broader than those values obtained in the polymerization of styrene. This could be ascribed to some side reactions or the relative rate of degenerative transfer was slightly lower than for styrene. The rate of degenerative transfer, however, is not significantly lower than that of propagation, for if this were the case, the molecular weight of the polymer would not increase with conversion. This happens in the polymerization of methyl methacrylate (Figure 13), where the molecular weight of the polymer did not grow with conversion. In the case of vinyl acetate, no polymer was obtained.

Conclusion. The controlled polymerization of styrene, methyl acrylate, and butyl acrylate has been achieved through degenerative transfer. This process required the use of a transfer agent which was capable of transferring an atom or group, X, to a propagating radical to form a dormant polymer chain. This polymer chain could then be reactivated by transferring the atom/group, X, to another propagating polymer chain, and in the process re-forming the original propagating center which reinitiated the polymerization. Described in this paper was the successful use of iodine as the X group and the compounds 1-phenylethyl iodide, iodoform, and iodoacetonitrile in particular. To a lesser degree, the perfluoroisopropyl and perfluorohexyl iodide compounds were also successful. The polymerization of styrene was well controlled, resulting in polymers with predicted molecular weights and low polydispersities. However, control of the polymerization of the acrylates was limited to molecular weight, while the polydispersities of the polymers were broader than for styrene, probably due to relatively slower degenerative transfer or unidentified side reactions.

Experimental Section

Styrene, methyl methacrylate, and methyl acrylate were obtained from Aldrich and stored over calcium hydride and distilled under vacuum prior to use. The distillate was then degassed by the freeze–pump–thaw method. Butyl acrylate was obtained from Eastman Kodak and was purified in a similar manner. The initiators, BPO and AIBN, were recrystallized from ether and were dried at room temperature under vacuum. All other reagents were used as obtained from Aldrich. Conversions were determined by measurement of residual monomer, with THF as an internal standard, using a Shimadzu GC-14 gas chromatagraph with a Shimadzu CR501 Chromatapac. The column used was a J&W Scientific 30 m DB-WAX Megabore (0.53 mm i.d.) column. Molecular weights were obtained by GPC of the sample using a Waters 712 WISP autosampler, Waters 510 HPLC pump, and Waters 410 differential refractometer. The samples were passed through four PHENOGEL columns (100 Å, 1000 Å, linear, and guard) in series. The molecular weights were determined by comparison with polystyrene standards. ^{1}H NMR spectra were obtained using a Bruker AM 300 spectrometer.

Synthesis of 1-Phenylethyl Iodide. Hexadecyltributylammonium bromide (0.1 equiv) was added to a stirring, biphasic mixture of styrene (1 equiv) and 47% hydroiodic acid (3–4 equiv). The solution was stirred for 4–8 h at 40 °C. As the reaction proceeded, the organic layer, originally colorless and above the aqueous layer, turned dark red and eventually became the lower layer with the aqueous layer above. ^{1}H NMR

Table 2. Various Monomers Polymerized in the Presence of 1-Phenylethyl Iodide

monomer	initiator	time (h)	conv	M_n theory/found	polydispersity
styrene[a]	AIBN	16	94	6580/7810	1.5
butyl acrylate[b]	AIBN	6.5	94	7320/9160	2.1
		4.0	85	4470/4870	2.0
		7.5[f]	98	5000/4610	1.9
		7.5[f]	97	18000/19300	2.0
		7.0[f]	95	2500/2820	1.6
methyl acrylate[c]	AIBN	2.0	35	3360/4640	1.9
methyl methacrylate[d]	AIBN	2.0	54	5080/18800	2.10
vinyl acetate[e]	AIBN	4	no polymer	–	–

[a] $[\text{Styrene}]_0$ = 8.74 M (bulk), $[\text{AIBN}]_0$ = 0.03 M, $[\text{1-phenylethyl iodide}]_0$ = 0.1 M, 70 °C. [b] $[\text{Butyl acrylate}]_0$ = 6.95 M (bulk), $[\text{AIBN}]_0$ = 0.03 M, $[\text{1-phenylethyl iodide}]_0$ = 0.1 M, 50 °C. [c] $[\text{Methyl acrylate}]_0$ = 11.06 M (bulk), $[\text{AIBN}]_0$ = 0.03 M, $[\text{1-phenylethyl iodide}]_0$ = 0.1 M, 50 °C. [d] $[\text{Methyl methacrylate}]_0$ = 9.36 M (bulk), $[\text{AIBN}]_0$ = 0.03 M, $[\text{1-phenylethyl iodide}]_0$ = 0.1 M, 60 °C. [e] $[\text{Vinyl acetate}]_0$ = 10.45 M (bulk), $[\text{AIBN}]_0$ = 0.03 M, $[\text{1-phenylethyl iodide}]_0$ = 0.1 M, 50 °C. [f] Solution polymerization in benzene.

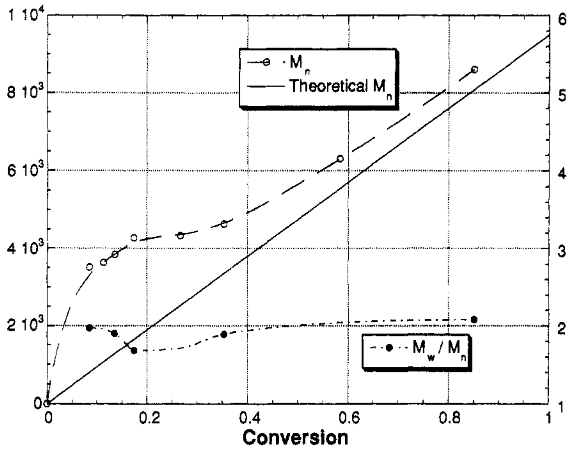


Figure 11. Dependence of M_n upon conversion for the bulk polymerization of methyl acrylate. $[\text{1-PEI}]_0$ = 0.1 M, $[\text{AIBN}]_0$ = 0.03 M.

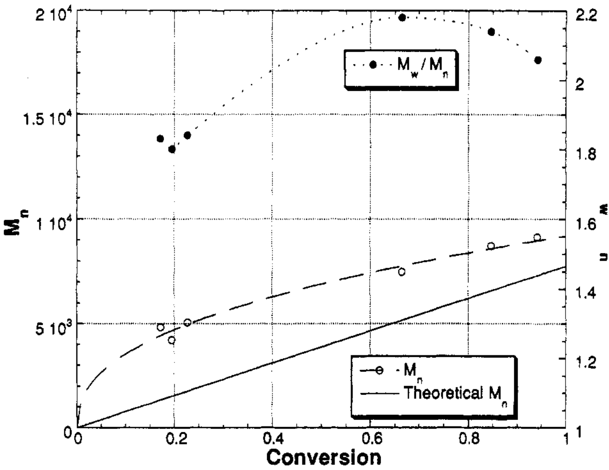


Figure 12. Dependence of M_n upon conversion for the bulk polymerization of butyl acrylate. $[\text{1-PEI}]_0$ = 0.1 M, $[\text{AIBN}]_0$ = 0.03 M.

showed that conversion of the styrene to the Markovnikov addition product, 1-phenylethyl iodide, was greater than 90%. The mixture was then separated and the aqueous layer washed with 3 × 25 mL of CH_2Cl_2. The organic layers were then combined and washed with the following: 25 mL of H_2O, 3 × 25 mL of saturated Na_2CO_3, 3 × 25 mL of H_2O. The organic layers were then combined and dried over sodium sulfate and subsequently evaporated to leave a dark red oil. This was purified by flash chromatography with hexanes through silica gel to give a pale yellow solution. Evaporation of hexanes gave a yellow oil, which was found to be light sensitive and stored in the dark at <0 °C. ^{1}H NMR ($CDCl_3$) δ 7.4–7.15 (m, 5H, Ar), 5.4 (quint, 1H, *J* = 7 Hz), 2.2 (d, 3H, J = 7 Hz) ppm.

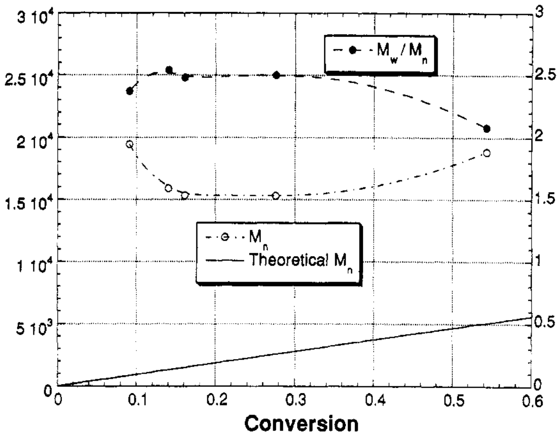


Figure 13. Dependence of M_n upon conversion for the bulk polymerization of methyl methacrylate. $[\text{1-PEI}]_0$ = 0.1 M, $[\text{AIBN}]_0$ = 0.03 M.

General Procedure for Polymerization. AIBN (0.0246 g, 0.15 mmol, $[I]_0$ = 0.03 M) was added to a test tube and then sealed with a rubber septum. Styrene (5 mL) was then added to the test tube via syringe. 1-Phenylethyl iodide (0.070 mL, 0.1160 g, 0.5 mmol, $[X]_0$ = 0.1 M) was finally added via syringe. The solution was then degassed by the freeze–pump–thaw method. Samples (0.5 mL) were then transferred to test tubes sealed with rubber septa, previously degassed and backfilled with argon. These samples were then immersed in an oil bath and removed at various times to monitor conversion and molecular weight. Upon removal from the oil bath, the samples were dissolved in 2.5 mL of THF. The resulting solutions were used for residual monomer analysis and determination of molecular weight of the obtained polymer.

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