

Living carbocationic polymerization of isobutylene and synthesis of ABA block copolymers by conventional laboratory techniques

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SUMMARY

Living polymerization of isobutylene (IB) and subsequent controlled synthesis of ABA block copolymers, such as poly(styrene-*b*-isobutylene-*b*-styrene) (PSt-PIB-PSt) and poly(*p*-methylstyrene-*b*-isobutylene-*b*-*p*-methylstyrene) (PpMeSt-PIB-PpMeSt), have been carried out by a simple and inexpensive conventional laboratory technique. The homo- and block copolymers obtained by using this technique have exhibited excellent molecular weight control and low polydispersity indexes. The living nature of IB polymerization has been demonstrated by the incremental monomer addition (IMA) method with the dicumyl methyl ether (DiCumOMe)/TiCl₄ initiating system in the presence of 2,5-di-*tert*-butylpyridine (DtBP) proton trap. PSt-PIB-PSt and PpMeSt-PIB-PpMeSt block copolymers have been synthesized by sequential monomer addition: first living difunctional polyisobutylene (PIB) midsegment was prepared by difunctional initiator, then the second monomer was added to the charge. High blocking efficiencies and desired block copolymer structures have been obtained.

INTRODUCTION

There is an ongoing significant interest in olefin and vinyl monomer based homopolymers, block and graft copolymers with well defined architecture in academia as well as in industry worldwide. The synthesis of such polymers with controlled molecular weight and molecular weight distribution (MWD) has been possible by living anionic polymerization since the mid 1950s¹. The discovery of group transfer polymerization (GTP)² in the early 1980s, and then living carbocationic³ and ring opening metathesis⁴ polymerizations in the mid 1980s has significantly expanded the synthetic opportunities for the preparation of tailor-made macromolecular systems from a large variety of olefins and vinyl monomers. For all these living polymerizations there is an important drawback in most cases: It is the necessity to work under extremely pure conditions, using dry and high purity solvents and reagents in order to obtain desired results and end products. Consequently special procedures and equipments are usually required to exclude all undesired impurities. For instance, the use of laborious special all-glass equipments and reactors in connection with high vacuum lines and breakseals between reservoirs has been required for several polymerization systems. Another possibility of avoiding impurities is the use of dry-boxes (stainless steel enclosure, glove-box) filled with dry inert gas such as nitrogen or argon. These equipments provide the inertness necessary for impurity sensitive polymerizations, but these are unfortunately costly setups as well.

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Living carbocationic polymerization has remarkably broadened the scope of carbocationic techniques for the synthesis of well-defined unique polymeric systems (see Refs. 5 and 11 for recent comprehensive overviews). It has been found that living carbocationic polymerization of olefins initiated by oxygen containing initiators, such as tertiary esters^{3d} and ethers^{3e}, or various initiators in the presence of a wide variety of externally added electron donors⁵ or a proton trap (*DtBP*)^{5,7} are much less sensitive to protogenic impurities than conventional cationic polymerizations of olefins. Such living polymerizations nevertheless are generally carried out by the use of special polymerization equipments such as dry-boxes and high vacuum line reactors. In this paper, we demonstrate that inexpensive, easy-to-handle conventional laboratory apparatuses and operations in open air (laboratory hood) is also suitable for successfully carrying out living carbocationic polymerization. This study also concerns living polymerization of IB by various initiators, the synthesis of narrow MWD telechelic polyisobutylenes (PIB), and preparation of narrow MWD PSt-PIB-PSt and PpMeSt-PIB-PpMeSt ABA block copolymers by sequential monomer addition.

EXPERIMENTAL

A. Materials

CH_2Cl_2 (Bie & Berntsen) was refluxed over CaH_2 for 24 hours before distillation, then Et_3Al was added and it was distilled before use. Methylcyclohexane (MeCHx) (Aldrich) was refluxed with cc. H_2SO_4 for 12 hours, washed to neutral with water, dried with MgSO_4 , and distilled from CaH_2 prior to use. Cumyl methyl ether (CumOMe), dicumyl methyl ether (DiCumOMe) and *tert*-butyl-*m*-dicumyl methyl ether (*tBumDiCumOMe*) were synthesized and purified as described elsewhere^{3e,6a,b,10c}. TiCl_4 (Aldrich) was distilled from CaH_2 under dry nitrogen atmosphere. *DtBP* (Aldrich) and anhydrous *N,N*-dimethylacetamide (DMA) (Aldrich) were used as received. Isobutylene (Hydro Gas Danmark) was passed through a column filled with barium oxide and molecular sieves before condensation. Styrene(St) (Aldrich) and *p*-methylstyrene(pMeSt) (Aldrich) were stirred with CaH_2 for 3 days, then vacuum distilled and kept in a freezer. They were redistilled under reduced pressure on the day of polymerization.

B. Equipments and Procedures

The basic component in our polymerization setup is a manifold as exhibited in Figure 1. It is built from two lines, one for nitrogen (passed through a column containing barium oxide and 4 Å molecular sieves for drying) and one for vacuum. Each piece has a 10 mm outer diameter, medium wall tubing, which is connected via ten 8 mm Rotaflo type stopcocks (specified to 10^{-6} bar). Between two paired stopcocks a glass-piece made of 7 mm OD glass tubing makes the joint to a thick-walled TYGON® hose, which at the other end is fastened either to a needle-tubing connector or to a three-way stopcock on the reactor. All glasswares were cleaned carefully and dried in an oven at 150 °C for at least 12 hours before use. The syringes used were Perfectum hypodermic syringes (Aldrich) with stainless steel needles. Both parts were baked in an oven overnight and cooled to room temperature in a desiccator prior to use. The reactors were 100 or 500 mL one-neck, rubber septum or three-way stopcock closed round bottomed flasks equipped with magnetic stirring bars. Usually, the flasks were purged with dry nitrogen from the manifold and occasionally were also flamed on the outside prior to the experiment. IB was condensed via a Teflon hose equipped with

a valve and a stainless steel needle into a nitrogen purged measuring cylinder capped with a rubber septum at -78°C .

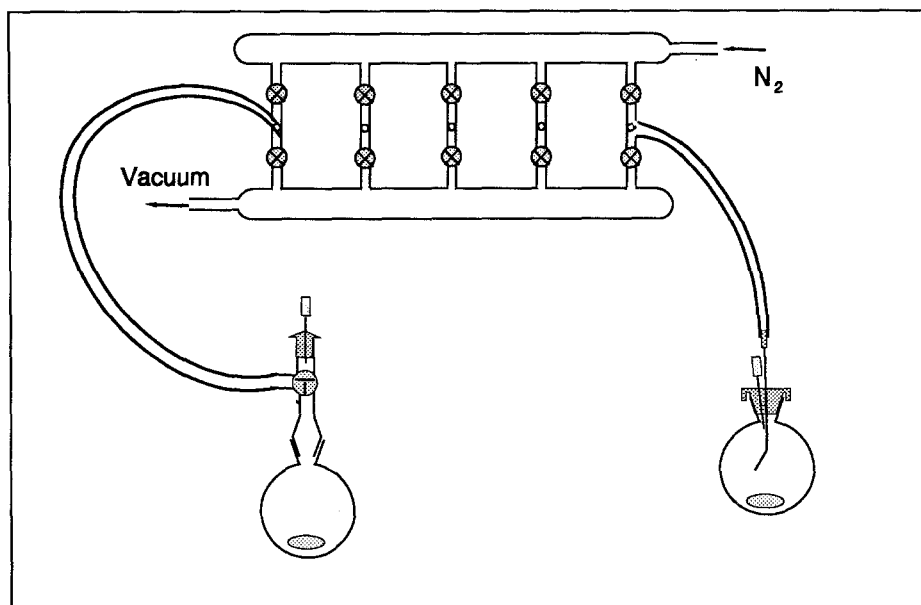


Figure 1. The manifold for inert atmosphere operations and two different polymerization reactor arrangements.

C. Polymerization

The solvents, CH_2Cl_2 and MeCH_x , and stock solutions of initiator and additives such as *D*tBP and DMA were transferred by syringes into the reactors. Then these mixtures were cooled by isopropanol/dry-ice bath to -78°C before IB was added via a double tipped stainless steel needle from the measuring cylinder. Polymerizations were induced by adding a predetermined amount of prechilled stock solution of TiCl_4 with a syringe. Prechilled methanol was used for quenching the polymerization. It is important to note that all components were transferred into the syringes by a slight nitrogen overpressure in order to minimize the contamination by moisture. When block copolymers were synthesized St or pMeSt was added with a syringe as a prechilled stock solution at predetermined time of IB polymerizations.

D. Polymer Characterization

The molecular weight of the polymers were measured by GPC (Waters pump model 910, Nucleosil columns $500\text{\AA} - 5\mu$, $200\text{\AA} - 5\mu$, $100\text{\AA} - 3\mu$, RI-detector) calibrated with PSt and PIB standards. St and the pMeSt contents in the block copolymers were determined gravimetrically, and by UV (Perkin-Elmer 320) and ^1H NMR (Bruker AC-250) spectroscopies.

RESULTS AND DISCUSSION

A. Living Polymerization of Isobutylene

The usefulness of the laboratory technique described in the Experimental was first tested by a series of preliminary IB polymerizations. As shown in Table I, various initiators were used in these polymerization experiments in conjunction with TiCl_4 coinitiator in the presence or absence of *DtBP* in $\text{CH}_2\text{Cl}_2/\text{MeCHx}$ (40:60 v/v) solvent mixtures. In the presence of *DtBP*, the addition of TiCl_4 to the polymerization charge resulted in a milky pale yellow precipitate. This is most likely due to the insoluble salt formed by protonation of *DtBP* by the low amount of moisture ($\sim 10^{-4} - 10^{-3}$ mol/L) present in the system as it has recently been concluded⁸. As the data in Table I indicate, isobutylene polymerization by the use of the experimental method developed in our laboratories results in high yields, 100% within experimental error in most cases, desired molecular weights, narrow MWD PIBs, and ~100% initiating efficiencies (I_{eff}).

Table I. Preliminary results of isobutylene polymerizations.

Initiator	Initiator M x 10 ⁻³	TiCl ₄ M x 10 ⁻²	<i>DtBP</i> M x 10 ⁻³	IB M	Solvent volume mL	Yield %	$M_n \times 10^{-3}$ (GPC)	M_w/M_n (GPC)	I_{eff} %
CumOMe	6.7	7.0	4.5	0.75	60	100	7.0	1.08	90
CumOMe	4.0	4.0	—	3.58	100	100	51.3	1.06	98
DiCumOMe	8.9	16.0	—	3.74	50	100	26.3	1.08	90
DiCumOMe	1.0	4.0	2.2	1.75	250	89	81.2	1.09	107
<i>t</i> BumDiCumOMe	3.6	5.8	5.3	1.54	50	90	23.5	1.06	92
<i>t</i> BumDiCumOMe	3.6	5.8	5.3	0.94	50	100	16.3	1.06	90

Reaction temperature: -78 °C; solvent: 40:60 v/v $\text{CH}_2\text{Cl}_2/\text{MeCHx}$; polymerization time: 20 mins.

Based on the satisfactory preliminary results further diagnostic experiments were carried out for living polymerization of IB by the IMA method^{3d,5}. Figure 2 shows the M_n and N/I_0 (inset) versus weight of polymer (W_p) plots obtained for the DiCumOMe/ TiCl_4 /IB polymerization system in the presence of *DtBP*. As exhibited in this Figure, M_n increases linearly with the increasing weight of the polymer formed in the consecutive monomer addition steps according to the theoretical line. As shown in the inset of Figure 2, the number of polymer chains (N) remains constant throughout the monomer addition increments in every 15 mins, and N is equal to I_0 , i.e., the number of initiator molecules (theoretical solid line). This indicates that under the experimental conditions used in this study detectable chain transfer to the monomer and/or uncontrolled initiation by impurities does not occur. M_w/M_n values as exhibited in Figure 2 in parentheses, slightly decrease as M_n increases. This finding is in line with the characteristics of living polymerizations, and it indicates that there is no permanent termination in this polymerization system. Recent kinetic studies⁸ are in accordance with this conclusion. Otherwise, that is in the presence of permanent termination, MWD broadening would be observed as M_n increases. The results of our experiments also indicate that relatively high molecular weight PIBs (up to $\sim 10^5$) can easily be prepared without difficulty by the use of the conventional experimental methods developed for these studies as described in the Experimental.

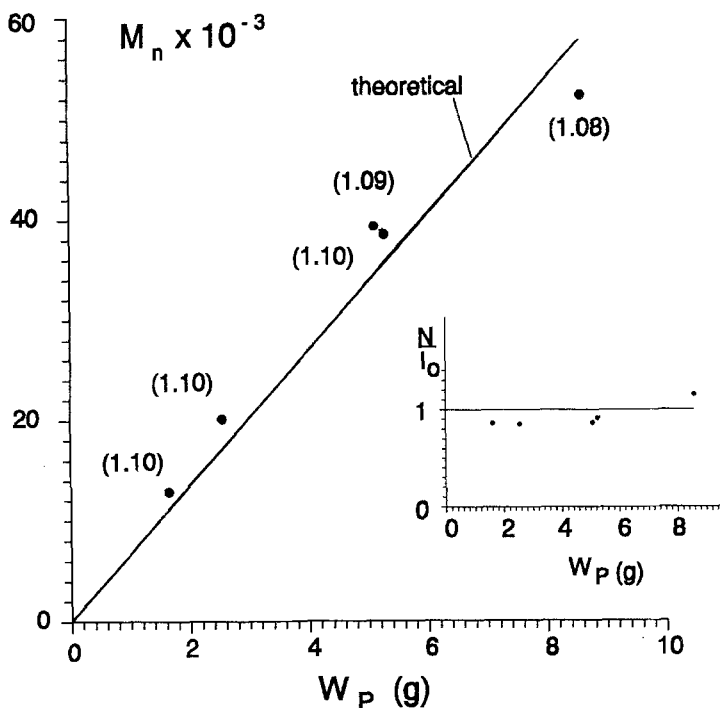


Figure 2. M_n and N/I_0 , the moles of polymer molecules formed per moles of initiator (I_0) (inset), as a function of W_p , weight of polymer, obtained by the IMA method for the DiCumOMe/TiCl₄/IB/DtBP/40:60 v/v CH₂Cl₂/MeCHx/-78 °C system (solid lines are theoretical); [DiCumOMe] = 2.96×10^{-3} M, [TiCl₄] = 6.0×10^{-2} M, [DtBP] = 5.94×10^{-3} M, $t = -78$ °C, $\Delta t = 15$ mins, $V = 50$ mL.

B. Synthesis of PSt-PIB-PSt and PpMeSt-PIB-PpMeSt ABA Block Copolymers

In living polymerizations di- or multi-functional initiators yield two or more growing chain ends, respectively. This is usually the basis for chain end functionalization in order to obtain telechelics (see Refs. 5, 6a,b, 10a-d, 11 on telechelic PIBs obtained by living carbocationic polymerization). The two- or multi-directional polymer growth can also be utilized to synthesize linear or starshaped block copolymers (for recent examples of PIB-based block copolymers obtained by living carbocationic polymerization see Refs. 5, 9a-f, 11). Thus, for example, ABA block copolymers can be prepared by adding a second monomer to PIB dications formed by initiation of IB polymerization with difunctional initiators, such as DiCumOMe, after consumption of IB in living carbocationic polymerization.

PSt-PIB-PSt and PpMeSt-PIB-PpMeSt ABA block copolymers have been synthesized by adding St and pMeSt, respectively, to polymerization charges containing PIB dications obtained by the DiCumOMe/TiCl₄ initiating system. Synthesis details and results are summarized in Table II and Figure 3. As this Figure indicates, there is a significant shift in the GPC traces toward higher molecular weights upon addition of the second monomer. Interestingly the significant broadening found in blocking of pMeSt to PIB in the presence

of triethyl amine (Et_3N)^{9e} has not been obtained under conditions used in our experiments, i.e., $\text{CH}_2\text{Cl}_2/\text{MeCHx}$ solvent mixture and presence of DfBP and DMA instead of $\text{CH}_3\text{Cl}/n$ -hexane and Et_3N . As the GPC traces in Figure 3 and the apparent polydispersity (A_w/A_n) of PpMeSt-PIB-PpMeSt in Table II show the molecular weight distribution of this block copolymer is nearly as narrow as that of the PIB midsegment's MWD. These findings indicate that PSt-PIB-PSt and PpMeSt-PIB-PpMeSt triblock copolymers can be successfully prepared by the conventional laboratory technique used in these studies (see Experimental). Indeed, extraction by methylethylketone (MEK), a good solvent for PSt and PpMeSt but a non-solvent for PIB , gave negligible amounts of extractables indicating nearly theoretical blocking efficiencies.

Table II. Synthesis conditions and characterization of PSt-PIB-PSt and PpMeSt-PIB-PpMeSt block copolymers.

	PIB midblock		Block copolymer			
	$M_{n,\text{GPC}}$	M_w/M_n	A_w/A_n	% PSt/PpMeSt (grav.)	% PSt/PpMeSt (UV)	% PSt/PpMeSt $^1\text{H NMR}$
PSt-PIB-PSt	75,200	1.10	1.07	34.5	20	32
PpMeSt-PIB-PpMeSt	55,000	1.07	1.08	16	14	nd

PSt-PIB-PSt : $[\text{DiCumOMe}] = 1.0 \times 10^{-3}\text{M}$, $[\text{DfBP}] = 1.8 \times 10^{-3}\text{M}$, $[\text{TiCl}_4] = 4.0 \times 10^{-2}\text{M}$, $[\text{i-C}_4\text{H}_8] = 1.43\text{M}$, $[\text{DMA}] = 5.0 \times 10^{-3}\text{M}$, $[\text{St}] = 0.35\text{M}$, $t = -78^\circ\text{C}$, polymerization time: 20 mins for IB and 30 mins for St.

PpMeSt-PIB-PpMeSt : $[\text{DiCumOMe}] = 2.5 \times 10^{-3}\text{M}$, $[\text{DfBP}] = 2.3 \times 10^{-3}\text{M}$, $[\text{TiCl}_4] = 4.0 \times 10^{-2}\text{M}$, $[\text{i-C}_4\text{H}_8] = 2.36\text{M}$, $[\text{DMA}] = 5.4 \times 10^{-3}\text{M}$, $[\text{St}] = 0.88\text{M}$, $t = -78^\circ\text{C}$, polymerization time: 20 mins for IB and 30 mins for pMeSt.

(nd = not determined)

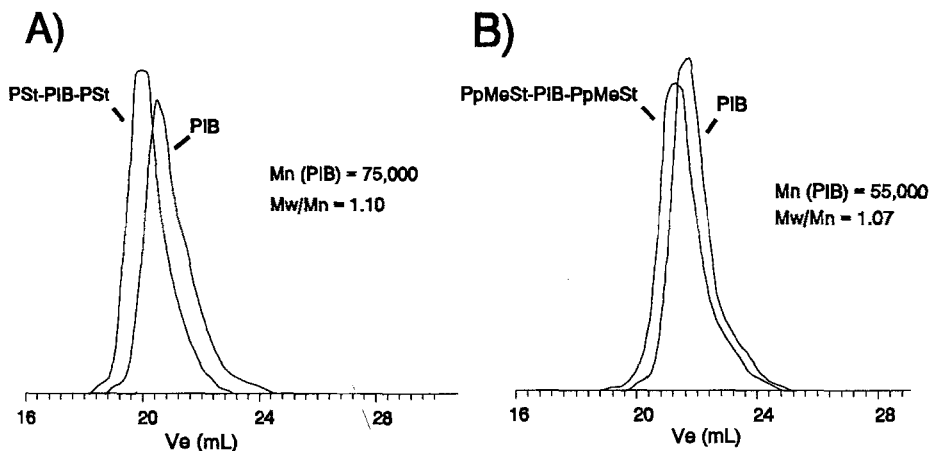


Figure 3. GPC traces of PIB midsegments, and PSt-PIB-PSt (A) and PpMeSt-PIB-PpMeSt (B) block copolymers obtained by living carbocationic polymerization (experimental conditions as in Table II).

CONCLUSIONS

Living carbocationic polymerization of IB and the subsequent controlled synthesis of PSt-PIB-PSt and PpMeSt-PIB-PpMeSt block copolymers have been successfully carried out by a conventional inexpensive laboratory technique developed in our laboratories. The results of these controlled polymerizations clearly indicate the low moisture sensitivity of living carbocationic polymerization of olefins under well-selected conditions. As a consequence, living carbocationic polymerizations with sufficient care, as described in the Experimental, can be successfully carried out in open air, e.g., in laboratory hoods. This easy-to-handle method is also useful for fundamental scientific investigations and for preparation of larger (at least laboratory scale) amounts of designed polymers by living carbocationic techniques. Thus by using this technique, PIB homopolymers, and PSt-PIB-PSt and PpMeSt-PIB-PpMeSt block copolymers with desired structures and narrow MWD have been prepared.

ACKNOWLEDGEMENTS

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