Cationic polymerization of hydrocarbon monomers induced by complexes of acyl halides with Lewis acids

11.* Synthesis of block copolymers of isobutylene with α-methylstyrene

V. B. Murachev, A. I. Nesmelov, E. A. Ezhova, and V. S. Byrikhin*

M. V. Lomonosov Moscow State Academy of Fine Chemical Technology,
86 prosp. Vernadskogo, 117571 Moscow, Russian Federation.
Fax: +7 (095) 430 7983

The block polymerization of isobutylene with α-methylstyrene induced by acyl initiators was investigated. The k_{el}/k_p values (the criterion for "closeness to the living state"), where k_{el} is the rate constant of proton elimination from a growing carbocation and k_p is the rate constant of chain growth, were analyzed. The minimum k_{el}/k_p values are characteristic of processes occurring in the presence of $PhCOCl \cdot 2AlBr_3$ and an equimolar mixture of $MeCOBr \cdot AlBr_3$ with $PhCOCl \cdot AlBr_3$. It was concluded that these complexes are efficient initiators for the synthesis of block copolymers with a relatively narrow molecular-weight distribution and a low content of homopolymers.

Key words: isobutylene, acyl halides, aluminum bromide, α-methylstyrene, block copolymers, cationic polymerization.

Earlier, we reported that the nature of R and the *n* value in acyl complexes $RCOX \cdot nAlBr_3$ (R is alkyl or aryl; X = Cl or Br; *n* = 1 or 2) used as initiators of the polymerization of isobutylene (IB) substantially affect the polymerization rate as well as the rates of chain transfer and termination, which characterize the tendency of a system to restriction. To estimate quantitatively the role of chain restriction reactions, the criterion for "closeness to the living state" was proposed,[2,3] which serves to choose a system that provides a polymer with a desired molecular weight and specific terminal groups. Moreover, the composition of an initiating system and the optimum conditions for the synthesis of block copolymers can be selected.

The synthesis of block copolymers with the use of living anionic systems, usually based on alkyllithium, has long been described.[4] The HI/I_2 system was successfully applied to prepare block copolymers of isobutyl vinyl ether with *p*-methoxystyrene,[5] and the ternary block copolymer poly(styrene-β-isobutylene-β-styrene) was synthesized in a *p*-dicumyl chloride—$TiCl_4$ system by using a particular technique of "quasi-living" carbocationic polymerization.[5] Many block copolymers possess the unique properties, and their formation under the action of the corresponding initiator seems to confirm the living character of active centers.[7]

In the present work, we attempted to use the criterion for "closeness to the living state" in choosing acyl systems for the synthesis of block copolymers of IB with α-methylstyrene (α-MS) and study some characteristics of such block copolymers.

Experimental

Purification and drying of the starting reagents and solvents, preparation of complexes, isolation and analysis of polymers, and an analysis of acyl complexes were described earlier.[8—10] The degree of conversion (*Q*) of monomers was determined by dilatometry or gravimetry (from a dry residue in the synthesis of block copolymers). Commercial pivaloyl chloride Me_3CCOCl was dried over PCl_5 and distilled in an atmosphere of argon. Polymerization was carried out in a all-glass vacuum unit at a residual pressure of 10^{-3} to 10^{-4} Torr and −78 °C in *n*-hexane.

To obtain block copolymers, the initial monomers were added in succession. A solution of IB in hexane was placed in a tube containing thin-walled balls filled with a solution of an initiator and a "bullet" (a small steel cylinder sealed in the glass cartridge). The tube was cooled to −78 °C, and the balls containing initiator were broken with the use of a magnet and the bullet, followed by immediate stirring of the content of the tube. The first step of polymerization lasted for 30—45 min. According to the data obtained from the previous runs, this time is needed to reach a nearly complete conversion of IB. After the first step, α-MS was added, and the polymerization was continued at the same temperature for an additional 30—45 min. The tube was opened, and the process was terminated by adding cooled MeOH (1 mL). The homopolymer of α-MS (PMS), insoluble in hexane, was separated on a pre-weighed filter, and the solution was poured into an excess of MeOH. Further purification of the precipitated polymer followed a common procedure. The composition of two-step polymerization products was determined using ^1H NMR spectroscopy and the ratio of the integral intensity of signals from aromatic and aliphatic protons ($CDCl_3$ as the solvent, Me_4Si as the internal standard).

In parallel, the process was carried out under similar conditions except that polymerization was terminated after the first step, and the resulting homopolymer of IB (PIB) was

---

* For Part 10, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 10, pp. 1944—1948, October, 1999.

further treated as a product of the first step of the two-step polymerization. Although such a procedure may cause some difference in the absolute indices of PIB samples obtained in two in-parallel runs, it allows one to exclude the influence of impurities inevitably introduced into the system when samples are withdrawn after the first step.

The degree of functionalization of polymers, *i.e.*, the fraction of macromolecules with the corresponding functional groups ($f_{C=O}$ and $f_{C=C}$), was calculated from IR data and ozonization as well as from the number-average molecular weight ($\bar{M}_n$) of these polymers (determined by gel-permeation chromatography, GPC).[8] The efficiency of initiation (E_{in}), *i.e.*, the part of the complex involved in initiation, was calculated from M_n of a polymer[9] and from IR and UV spectroscopic data. In the case of mixed complexes, the amount of MeCOBr, the acyl halide actually involved in initiation, was taken to determine E_{in}.

Results and Discussion

Among all the systems described earlier,[2,3] complex $PhCOCl \cdot 2AlBr_3$ (Bn-2) is characterized by the minimum k_{el}/k_p ratio ((2.3—7.5) $\cdot$ 10^{-6} mol L^{-1}), where k_{el} is the proton elimination rate constant and k_p is the chain growth rate constant. Therefore, this complex can be used as the most efficient initiator in the synthesis of block copolymers. The k_{el}/k_p value of acyl systems can also be reduced by introducing small amounts of electron-donor additives, *e.g.*, 2,6-dimethylpyridine.[2,11] However, we did not follow this method because, in addition to the search for optimum conditions for the synthesis of block copolymers, our study was aimed at verifying assumptions of a high viability resulting from the proposed criteria.

In the present work, an attempt was made to extend the earlier described complexes[1—3,8,9,12] to pivaloyl chloride complexes $Me_3CCOCl \cdot AlBr_3$ (Pv-1) and $Me_3CCOCl \cdot 2AlBr_3$ (Pv-2) and mixed acetyl-benzoyl complexes $MeCOBr \cdot AlBr_3$ + $PhCOCl \cdot AlBr_3$ (AcBn-1) and $MeCOBr \cdot 2AlBr_3$ + $PhCOCl \cdot 2AlBr_3$ (AcBn-2) and in this way to search for the most efficient acyl systems for the synthesis of block copolymers.

Complex Pv-1 does not initiate the polymerization of IB (the degree of conversion Q = 0, Table 1). This correlates with its ^1H NMR spectral pattern (no signals from acidic protons at δ 3.5—4.7 characteristic of acetyl complexes).[5,13] The ^{13}C NMR spectrum does not contain a signal at δ 150 inherent in the salt structures of such complexes.[10,13] In contrast, complex Pv-2 is highly active and its efficiency index of initiation (E_{in} = 31.2%) is the highest among the corresponding values of the complexes studied. Nevertheless, complex Pv-2 is hardly suitable for the synthesis of block copolymers because of an increased tendency of carbocations to eliminate protons (k_{el}/k_p = $1.7 \cdot 10^{-4}$ mol L^{-1}).

A much more "living" character of polymerization is observed for mixed acetyl-benzoyl complexes, especially AcBn-1. Its k_{el}/k_p value ($1.3 \cdot 10^{-5}$) is close to that of complex Bn-2, which is very efficient in polymerization. According to IR and UV data, the initiating particles of these complexes are exclusively acetylium cations ($f_{C=O}$ = ~100%), while benzoyl complexes seem to play a modifying role. The mechanism of chain restriction in the systems with these mixed complexes is the same as in the systems with Ac-2 and Bn-2,[9,10] which is why the same criterion, k_{el}/k_p, may be used as a measure of "closeness to the living state" for systems with the initiating complexes AcBn-1 and AcBn-2.[2]

Thus, in addition to the known complex Bn-2, complex AcBn-1 may be proposed as an initiator for preparation of block copolymers. However, it should be emphasized that a high viability of active centers characteristic of these initiators in the polymerization of IB will also be retained in the polymerization of α-MS. In some cases, chain termination or transfer is especially pronounced at the beginning of formation of the second (or next) block,[14] *i.e.*, when a living prepolymer reacts for the first time with molecules of the second monomer. For comparison, in subsequent runs we also used the acetyl complex $MeCOBr \cdot 2AlBr_3$ (Ac-2), characterized by a moderate tendency to form living active centers in the polymerization of IB.[2]

Table 1. Results of the polymerization of isobutylene induced by acyl complexes in hexane at −78 °C[a]

Composition of the complex	Polymer				E_{in}	k_{el}/k_p
	Q (%)	$\bar{M}_n \cdot 10^{4}$	$\bar{M}_w/\bar{M}_n$	$f_{C=C}$ (%)	(%)	/mol L^{-1}
$Me_3CCOCl \cdot AlBr_3$ (Pv-1)	0	—	—	—	—	—
$Me_3CCOCl \cdot 2AlBr_3$ (Pv-2)	~100	5.62	2.05	34	31.2	$1.7 \cdot 10^{-4}$
$MeCOBr \cdot AlBr_3$[b] + $PhCOCl \cdot AlBr_3$ (AcBn-1)	71	33.70	1.61	6	3.7	$1.3 \cdot 10^{-5}$
$MeCOBr \cdot 2AlBr_3$[b] + $PhCOCl \cdot 2AlBr_3$ (AcBn-2)	~100	12.40	2.01	10	14.1	$2.3 \cdot 10^{-5}$

[a] Experimental conditions: [IB] = 2.35 mol L^{-1}, [RCOX] = 7.5 mmol L^{-1}, 15 min.
[b] Equimolar mixtures; in these runs, [RCOX] = [MeCOBr].

The results of the first step of block copolymerization, leading to the formation of a living PIB prepolymer (Table 2), differ somewhat from the published data on the polymerization of IB in the presence of Bn-2[10] (see Table 1) for the mixed complex AcBn-1. This difference is probably due to the different conditions of polymerization. In our experiments, the concentrations of initiating complexes were about ten times higher than the common ones. Presumably, this could yield lower-molecular products and decrease the viscosity, thus facilitating the introduction of a second monomer and enhancing the accuracy of an analysis for the content of terminal groups. When passing to high concentrations of complexes, their k_{el}/k_p values increase by a factor of 3 to 5, and at least two effects we previously ignored deserve consideration. First, at a higher rate of the process its isothermic character can be violated. Second, active centers in the cationic polymerization of IB in nonpolar solvents tend to be associated.[15] For many initiating systems used in anionic[4,16] and ionic-coordination[17,18] polymerization, it was shown that the rate constants of separate polymerization stages and, in some cases, the stereoregulating ability differ markedly for associated and nonassociated forms of active centers. It is quite probable that the differences observed may be also due to the existence of two forms of active centers. Nevertheless, the order of decreasing k_{el}/k_p ratio in the series Ac-2 > AcBn-1 > Bn-2, which corresponds to increasing viability of the system, is also retained in the synthesis of a prepolymer (but only at low concentrations of the complexes).

The results of the second stage of synthesis of a block copolymer, *i.e.*, the formation of poly-α-methylstyrene block, are given in Table 3. To control the efficiency of this step, the final product was analyzed by GPC following separation from a homopolymer of α-MS. Additional information on the composition of the product was obtained by ^{1}H NMR spectroscopy. It was assumed that the reaction of living PIB with introduced α-MS should give a mixture of homopolymers, and the chromatograms and spectra of a hexane-soluble product and a prepolymer would be virtually identical, provided that the chain transfer to a second comonomer is crucial at the beginning of the process. If chain termination is a decisive factor at this stage, a PIB prepolymer (probably, with a small content of α-MS fragments) rather than an α-MS homopolymer (PMS) will be a soluble product. Finally, in the case of effective formation of a block copolymer, its peak should appear in the high-molecular region of a chromatogram, while that of a prepolymer should disappear.

Unfortunately, the viability of active cationic centers cannot be estimated directly in the homopolymerization of α-MS. The resulting polymer is not soluble in aliphatic solvents, which can cause "physical termination" following occlusion of the active centers in the precipitated product. This is also the reason why the choice of the total ratio of the monomers added in the first and second stages was limited. When the length of a polymethylstyrene block is excessive, molecules of a block copolymer should precipitate.

The chromatograms of the polymers synthesized are shown in Fig. 1. All the initial polymers had a unimodal molecular-weight distribution (MWD), though the MWD for a prepolymer formed under the action of Ac-2 is

Table 2. Results of the synthesis of the PIB prepolymer in the first step of block copolymerization

Sample	Initiator	Reaction time /min	PIB prepolymer				E_{in} (%)	k_{el}/k_p /mol L^{-1}
			Q (%)	$f_{C=C}$ (%)	$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_w/\bar{M}_n$		
2—1	Ac-2[a]	30	93	31	20.1	3.2	5.2	$2.4 \cdot 10^{-4}$
2—2	Bn-2[b]	45	~100	4	18.5	2.1	9.7	$2.1 \cdot 10^{-5}$
2—3	AcBn-1[a]	45	96	9	33.7	2.4	3.2	$3.6 \cdot 10^{-5}$

Note. Experimental conditions: hexane, −78 °C, [IB] = 0.80 mol L^{-1}.
[a] C = 40 mmol L^{-1}. [b] C = 25 mmol L^{-1}.

Table 3. Results of the second step of block copolymerization

Sample	Initiator	Reaction time/min	Q(α-MS) (%)	Fraction of PMS[a] (%)	IB/α-MS[b]	$\bar{M}_n$ (calc) $\cdot 10^{-3}$	$\bar{M}_n$(GPC) $\cdot 10^{-3}$	$\bar{M}_w/\bar{M}_n$ (GPC)
3—1	Ac-2	30	35	34	4.87	30.5	27.6	4.7
3—2	Bn-2	45	75	0	1.90	39.0	44.0	2.4
3—3	AcBn-1	45	70	11	2.07	68.0	74.0	2.6

Note. Hexane, −78 °C, [α-MS] = 0.54 mol L^{-1}.
[a] The fraction of the homopolymer α-MS with respect to the polymerized α-MS.
[b] The ratio between IB and α-MS fragments in a block copolymer, calculated from ^{1}H NMR spectral data with allowance for the number of IB fragments in dead PIB (the amount of the latter is determined by $f_{C=C}$, the fraction of macromolecules with terminal C=C bonds in the prepolymer).

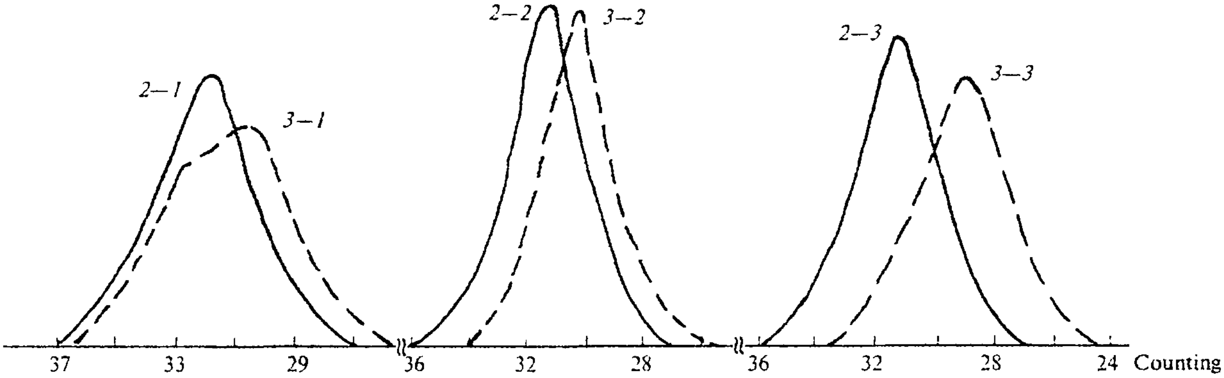

Fig. 1. Gel chromatograms of polymers after the first (solid line) and second step (dotted line) of polymerization; toluene as the solvent (numbering corresponds to that in Tables 2 and 3).

distinctly broader. Such a distribution is in good agreement with high $k_{\rm el}/k_{\rm p}$ values for a system with Ac-2 and a high index of polydispersity, $\bar{M}_{\rm w}/\bar{M}_{\rm n}$, for the corresponding prepolymer (see Table 2). A shift of peaks to the high-molecular region after the second stage in all three systems indicates that the contribution of chain restriction does not increase when living blocks of PIB react with molecules of α-MS. The use of complexes Bn-2 and AcBn-1 affords products with unimodal MWD at the second step, which, as judged from a minor increase in the index of polydispersity (*cf.* Tables 2 and 3), were only slightly broader than the MWD of the initial prepolymers. These facts confirm that active carbocationic centers retain a high viability in the polymerization of α-MS. A good agreement between experimental $\bar{M}_{\rm n}$ values ($\bar{M}_n$(GPC)) and those calculated on the assumption of a "living" character of the process in the second stage, $M_{\rm n}$(GPC), correlates with the fact that the molecules of a prepolymer with terminal *tret*-Cl are involved in initiation. A bimodal character of the MWD of a polymer obtained in a system containing complex Ac-2 can be explained by an increased content (31%) of a "dead" PIB prepolymer in the product of the second stage. The $\bar{M}_{\rm n}$ and $\bar{M}_{\rm w}/\bar{M}_{\rm n}$ values given in Table 3 for this sample are rough because IB and α-MS fragments differ substantially in refraction index. Nevertheless, initiators Bn-2 and AcBn-1 selected from low $k_{\rm el}/k_{\rm p}$ values proved to be in fact the most efficient for the synthesis of block copolymers, for the yields of homopolymers in the presence of these initiators were minimum.

When a prepolymer obtained under the action of Bn-2 was used, PMS virtually was not detected. In a similar experiment with AcBn-1, the fraction of PMS was equal to only 11%. The formation of a small amount of a homopolymer of α-MS may be due to appearance of an additional number of active centers as a result of dilution of the mixture with a second monomer; this effect was observed by us earlier[9] in the study of a two-step polymerization of IB. However, in a system with Ac-2 the yield of the homopolymer is very high (the content of PMS amounts to 34%) and cannot be explained by such a "dilution effect." (Moreover, in similar experiments with the initiating acyl complexes AcBn-2 and $\rm Me_3C_6H_2COBr \cdot 2AlBr_3$, this content increases up to 70—73%.) Apparently, the polymerization of α-MS is accompanied by chain transfer reactions that are not characteristic of the homopolymerization of IB occurring under analogous conditions.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-32825a).

References

1. V. B. Murachev, A. I. Nesmelov, E. A. Ezhova, V. S. Byrikhin, A. V. Orlinkov, and I. S. Akhrem, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 52 [*Russ. Chem. Bull.*, 1998, **47**, 50 (Engl. Transl.)].
2. V. B. Murachev, A. M. Evtushenko, A. I. Nesmelov, E. A. Ezhova, A. V. Orlinkov, and I. S. Akhrem, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 745 [*Russ. Chem. Bull.*, 1997, **46**, 714 (Engl. Transl.)].
3. V. B. Murachev, A. V. Orlinkov, A. I. Nesmelov, E. A. Ezhova, V. S. Byrikhin, and I. S. Akhrem, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1147 [*Russ. Chem. Bull.*, 1997, **46**, 1099 (Engl. Transl.)].
4. M. Szwarc, *Carbanions, Living Polymers and Electron Transfer Processes*, Interscience, New York, 1968.
5. M. Sawamoto, T. Ohtayo, T. Higashimura, K.-H. Guhrs, and G. Heublein, *Polym. J.*, 1985, **17**, 929.
6. Zs. Fodor, J. P. Kennedy, N. Kelen, and F. Tudos, *J. Macromol. Sci., Chem.*, 1987, **A24**, 735.
7. R. P. Quirk and B. Lee, *Polym. Int.*, 1992, **27**, 359.
8. A. I. Nesmelov, A. V. Orlinkov, V. B. Murachev, I. S. Akhrem, V. S. Byrikhin, and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2232 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 2006 (Engl. Transl.)].
9. A. I. Nesmelov, A. V. Orlinkov, V. B. Murachev, I. S. Akhrem, V. S. Byrikhin, and V. P. Zubov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2506 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 2266 (Engl. Transl.)].

10. V. B. Murachev, A. I. Nesmelov, V. S. Byrikhin, E. A. Ezhova, A. V. Orlinkov, I. S. Akhrem, and M. E. Vol'pin, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1175 [*Russ. Chem. Bull.*, 1996, **45**, 1115 (Engl. Transl.)].
11. A. I. Nesmelov, V. B. Murachev, E. A. Ezhova, S. I. Tregubenkov, V. S. Byrikhin, A. V. Orlinkov, and I. S. Akhrem, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1180 [*Russ. Chem. Bull.*, 1996, **45**, 1120 (Engl. Transl.)].
12. V. B. Murachev, E. A. Ezhova, A. I. Nesmelov, V. S. Byrikhin, A. V. Orlinkov, and I. S. Akhrem, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 974 [*Russ. Chem. Bull.*, 1997, **46**, 934 (Engl. Transl.)].
13. A. V. Orlinkov, I. S. Akhrem, and M. E. Vol'pin, *Usp. Khim.*, 1991, **60**, 1049 [*Russ. Chem. Rev.*, 1991, **60** (Engl. Transl.)].
14. S. K. Varshney, C. Jacobs, J.-P. Hautekeer, Ph. Bayard, R. Jérôme, R. Fayt, and Ph. Teyssié, *Macromolecules*, 1991, **24**, 4997.
15. V. B. Murachev, A. I. Nesmelov, I. V. Kalyutich, V. A. Speranskii, and V. S. Byrikhin, *Vysokomol. Soedin., Ser. B*, 1995, **37**, 698 [*Polym. Sci.*, *B*, 1995, **37**, 166 (Engl. Transl.)].
16. A. A. Arest-Yakubovich, I. V. Zolotareva, N. I. Pakuro, E. V. Kristal'nyi, and B. I. Nakhmanovich, *Vysokomol. Soedin., Ser. A*, 1996, **38**, 418 [*Polym. Sci.*, *A*, 1996, **38** (Engl. Transl.)].
17. B. A. Dolgoplosk and E. I. Tinyakova, *Metalloorganicheskii kataliz v protsessakh polimerizatsii* [*Organometallic Catalysis in Polymerization Processes*], Nauka, Moscow, 1982, 153 (in Russian).
18. M. V. Terganova, V. B. Murachev, I. F. Varlamova, N. N. Luzina, V. S. Byrikhin, and A. N. Pravednikov, *Vysokomol. Soedin., Ser. B*, 1981, **23**, 473 [*Polym. Sci. USSR*, 1981, **23** (Engl. Transl.)].

Received December 18, 1998