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

6.* The effect of 2,6-dimethylpyridine on the polymerization of isobutylene

A. I. Nesmelov,[a*] *V. B. Murachev,*[a*] *E. A. Ezhova,*[a] *S. I. Tregubenkov,*[a] *V. S. Byrikhin,*[a]
A. V. Orlinkov,[b] *and I. S. Akhrem*[b]

[a]*M. V. Lomonosov Moscow State Academy of Fine Chemical Technology,*
86 prosp. Vernadskogo, 117571 Moscow, Russian Federation.
Fax: +7 (095) 430 7983
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

The effect of 2,6-dimethylpyridine on the cationic polymerization of isobutylene in *n*-hexane and dichloromethane at −78 °C under the action of complexes of acetyl bromide with $AlBr_3$ of the compositions 1 : 1 and 1 : 2 was investigated. 2,6-Dimethylpyridine significantly depresses the initiation and chain transfer processes involving free protons and also retards the proton elimination from growing carbocations.

Key words: isobutylene, polyisobutylene, molecular weight, molecular weight distribution, end groups; Lewis acids, cationic polymerization.

Previously[1] we have shown that the use of the complex of acetyl bromide with aluminum bromide of the composition 1 : 2 (complex Ac-2) as the initiator of the cationic polymerization of isobutylene (IB) in hexane at −78 °C allows one to obtain polyisobutylene (PIB) in which virtually all the macromolecules contain head acetyl groups (the degree of functionalization $f_{C=O} \approx 100$ %). Since the concentration of end C=C groups ($f_{C=C}$) in the polymer can reach relatively large values of up to 47 %,[2] it was concluded that virtually no direct chain transfer to the monomer occurs in this system, while the indirect chain transfer is interrupted after the first step yielding the intermediate "superacid" $HBr \cdot 2AlBr_3$.

Studies devoted to the cationic polymerization of vinyl monomers in the presence of electron-donating compounds have been discussed in detail in the literature.[3] In the present paper we report on the polymerization of IB through the action of acetyl complexes of aluminum bromide in the presence of n-electron-donating 2,6-dimethylpyridine (lutidine, 2,6-DMP). It has been of interest both from the theoretical and practical viewpoint to study the possibility of more complete depression of chain transfer by electron-donating additives (*i.e.*, of bringing the process closer to the "living" polymerization) in the systems studied by us where the process is initiated by acyl complexes. The choice of 2,6-DMP is due, among other reasons, to the fact that its structure is similar to that of the typical "proton trap," namely, 2,6-di-*tert*-butylpyridine (DTBP) used for controlling polymerization of hydrocarbon monomers and for elucidating its mechanism.[4—6] This similarity allowed us to consider in more detail the factors determining the mechanism of the action of these additives in individual steps of the cationic polymerization.

Experimental

The purification and drying of the starting reagents and solvents (*n*-hexane and dichloromethane), the procedures for the preparation of initiating complexes, conduction of the polymerization, isolation and analysis of the polymers, as well as for the calculation of the degree of functionalization, *i.e.*, the fraction of macromolecules with the corresponding functional groups ($f_{C=O}$, $f_{C=C}$, and f_{C-Br}), from the results of the analysis of the polymer samples were described previously.[1,2,7,8] The efficiency of initiating (E_{in}), defined as the ratio of the molar concentrations of the polymer and the initiator, was calculated from the equation presented in one of our communications.[2] The end groups in the polymeric molecules synthesized in the presence of acyl complexes, as has been shown in the previous experiments,[1,2] were always only C=C and C—Hal groups, *i.e.*, the ($f_{C=C} + f_{C-Br}$) sum was equal to 100 % to within the experimental error. For this reason, the complete analysis of the end groups was carried out only for separate check samples. According to the data of gel permeation chromatography, all the polymers obtained had unimodal molecular weight distribution (MWD).

---

* For Part 5, see *Russ. Chem. Bull.*, 1996, **45**, 1115 (Engl. Transl.).

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 5, pp. 1180—1183, May, 1996.

1066-5285/96/4505-1120 $15.00

2,6-Dimethylpyridine was distilled, held over 4Å molecular sieves, degassed, and recondensed *in vacuo*.

Results and Discussion

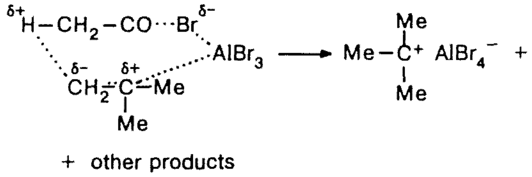
The data presented in Table 1 make it possible to estimate the effect of the addition of 2,6-DMP on the polymerization of IB in hexane induced by the acyl complex Ac-2. For all these polymers, $f_{C=O} \approx 100$ %, and the number average molecular weights ($\bar{M}_n$) of PIB in the presence and in the absence of 2,6-DMP increase linearly with an increase in the degree of conversion (Q) of the monomer. The introduction of 2,6-DMP decreases the efficiency of initiation by 20—30 %, but has only a slight effect on the rate of polymerization. The effect of this donor of electrons on the $f_{C=C}$ value is much more pronounced: its presence depresses to a large extent the elimination of a proton from the growing carbocation giving the end C=C groups. As a consequence, the considerable broadening of MWD at late stages of the polymerization, observed for this system containing no 2,6-DMP, is prevented. The narrowing of MWD is also one of the most typical consequences of the introduction of other electron donors[3] or proton traps[5] to cationic polymerizing systems. The increase in the livingness of the system in the presence of 2,6-DMP is also confirmed by the sharp (by an order of magnitude) decrease in the rate constant of the destruction (k_d) of active centers *via* the proton elimination, calculated by the procedure described in one of our previous papers:[9] $k_d = 3.3 \cdot 10^{-5}$ s^{-1} compared to $3.5 \cdot 10^{-4}$ s^{-1} for the same system in the absence of 2,6-DMP.[9]

Table 1. Study of the two-step polymerization of IB in hexane at −78 °C under the action of the complex Ac-2 without n-electron-donating compounds added and in the presence of 2,6-DMP ($[IB]_0 = 1.25$ mol L^{-1}, [Ac-2] = 4.1 mol L^{-1})[a]

t/min	Q (%)	Polymer[b]				E_{in} (%)
		$\bar{M}_n \cdot 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$f_{C=C}$ (%)	f_{C-Br} (%)	
			[2,6-DMP] = 0			
			The first step			
2	28	44.8	1.62	4.1	98.3	10.7
5	53	96.8	2.16	11.4	—	9.3
20	94	151.0	3.43	26.0	72.7	10.7
25	98	157.4	3.09	31.0	—	10.6
			The second step[c]			
36	52[d]	213.4	3.95	44.0	52.2	12.2
60	75[d]	202.3	5.07	47.2	—	14.8
			[2,6-DMP] = 0.5 mmol L^{-1}			
			The first step			
5	42	86.9	1.56	1.0	97.7	8.3
50	99	208.0	1.62	9.0	—	8.2
			The second step[e]			
55	37[d]	276.0	1.70	10.1	92.6	8.5
100	89[d]	384.0	1.72	16.9	—	8.4

[a] Equal amounts of the monomer were introduced in the first and in the second step. [b] For all the polymer samples obtained, $f_{C=O} \approx 100$ %. [c] The second portion of the monomer was introduced during the 30th min. [d] The degree of conversion Q in the second step was calculated with respect to the second portion of the monomer, the conversion of the first portion being assumed to be 100 %. [e] The second portion of the monomer was introduced during the 50th min.

An effect of 2,6-DMP on the polymerization of IB in hexane under the action of the equimolar complex of acetyl bromide with aluminum bromide (Ac-1) has been found previously,[1] although it has not been discussed in detail. For [IB] = 1.4 mol L^{-1}, [Ac-1] = 7.5 mmol L^{-1}, and [2,6-DMP] = 1.9 mmol L^{-1}, the yield of PIB over a period of 2 h was only 17 %, whereas under similar conditions in the absence of 2,6-DMP, the IB was quantitatively converted already after 30 min.[1] These results confirm the proton-producing activity of Ac-1 in the initiation of the polymerization of IB. At the same time, taking into account the absence of end acetyl groups in the PIB samples synthesized under the action of this complex ($f_{C=O} = 0$), one may believe that in this case, the proton initiation partly occurs by a way of concerted mechanism[5] without isolation of free protons:



Judging by the dramatic decrease in the yield of PIB in the presence of 2,6-DMP, the contribution of the concerted mechanism to the general scheme of initiation under normal conditions (without lutidine) is not very large, no more than 5—10 %.

On going to a more polar solvent, namely, dichloromethane, the rate of the Ac-2-initiated polymerization of IB increases, and the MWD narrows down.[7] In this case, only <50 % of the macromolecules of PIB formed contain head C=O groups. A comparison of the $f_{C=O}$, $f_{C=C}$, and f_{C-Br} values for these polymers demonstrated both the appearance of proton-producing initiating activity of Ac-2 in a more polar medium and the possibility of an indirect chain transfer to the monomer in this case (*i.e.*, the occurrence of processes that are not realized in hexane and mostly involve free protons).

Based on the effects of 2,6-DMP on the polymerization of IB in hexane found, one may assume that in dichloromethane, too, the addition of this donor of electrons will suppress the processes occurring with the participation of protons. In fact, the data of Table 2 indicate that the introduction of 2,6-DMP decreases the rate of the polymerization of IB in dichloromethane under the action of Ac-2 and, especially, Ac-1 and, in the former case, it also increases dramatically the $f_{C=O}$ values of the polymers. In addition, in the presence of 2,6-DMP, the $f_{C=C}$ and E_{in} values and the polydispersion index $\bar{M}_w/\bar{M}_n$ decrease for the systems containing any of the two initiating complexes. In other words, the behavior of 2,6-DMP

Table 2. Study of the polymerization of IB in dichloromethane at −78 °C without n-electron-donating compounds added and in the presence of 2,6-DMP

Initiator	t/min	Q (%)	Polymer					E_{in} (%)
			$\overline{M}_n \cdot 10^{-3}$	$\overline{M}_w/\overline{M}_n$	$f_{C=O}$ (%)	$f_{C=C}$ (%)	f_{C-Br} (%)	
$[AcBr] = 8.55$ mmol L^{-1}, $[IB]_0 = 0.80$ mol L^{-1}, $[2,6\text{-DMP}] = 0$								
Ac-1	20	100	7.1	2.5	0	31	69	—
Ac-2	20	100	5.2	3.1	42	27	72	99.4
$[AcBr] = 6.40$ mmol L^{-1}, $[IB]_0 = 0.99$ mol L^{-1}, $[2,6\text{-DMP}] = 1.1$ mmol L^{-1}								
Ac-1	40	20	16.4	2.2	0	19	—	—
Ac-2	40	93	25.2	2.7	92	11	—	32.0

in polar and nonpolar media is qualitatively similar, regarding its effect on the processes determined by the participation of protons.

Consideration of the set of data presented above naturally brings up the question of whether 2,6-DMP should be regarded as an electron-donating additive or as a proton trap like DTBP? It is not as easy to answer this question as might be expected at first glance. In fact, fundamental studies[10,11] have shown that DTBP, being strongly basic but not nucleophilic due to steric restrictions, exhibits extremely high activity toward interaction with a proton but does not react with either BF_3 or methyl iodide. These features of the behavior of DTBP and some other compounds of this sort allowed them to be categorized as a specific class of "proton traps." However, some authors, while discussing the results of a series of studies on the polymerization of IB and α-methylstyrene in the presence of DTBP,[5] concluded that a certain sort of interaction (binding into complexes?) exists between this substituted pyridine with the growing carbocation. However, due to the lack of data, they were not able to state more particular considerations about the nature of this interaction. To the contrary, the authors of a recent paper[12] believe that the main function of the electron-donating additives during cationic polymerization is also the trapping of protons rather than "stabilization of the carbocations" as has been suggested previously.[13,14] In fact, suppression of the proton initiation and narrowing of the MWD are known to be typical consequences of the introduction of electron donors into polymerizing systems (see, for example, Ref. 15).

A study of the formation of complexes of $AlEt_3$ with nitrogen-containing electron-donating compounds has shown that the standard enthalpies for this process involving pyridine and 2,6-DMP are rather close (26.3 and 23.1 kcal mol^{-1}, respectively).[16] Thus, lutidine is capable of binding into complexes with aluminum-containing Lewis acids, which distinguishes it from classical proton traps like DTBP. At the same time, the fact that 2,6-DMP exhibits no inhibiting effect in the polymerization of IB initiated by acyl cations (see Table 1) indicates that the steric hindrance caused by the two methyl groups prevents the formation of a stable quaternary salt on the interaction with the growing carbocation. It is notable that triethylamine also does not cause the inhibition of the cationic polymerization of IB through the action of a cation-producing agent, 1,4-dicumyl alcohol, but prevents its initiation by proton-containing admixtures.[17]

Thus, the data presented in our paper clearly demonstrate that the processes involving free protons are suppressed by the addition of 2,6-DMP. However, some facts indicate that the role of lutidine extends further. In particular, the decrease in the $f_{C=C}$ value of the polymers and the corresponding tenfold decrease in k_d for the Ac-2 system in hexane in the presence of 2,6-DMP cannot be explained by the trapping of protons. The suggestion that the carbocation is stabilized by the electron-donating compounds added and, hence, the probability of the proton elimination decreases, seems more reasonable in this case. Note that the decrease in $f_{C=C}$ we found does not agree with the sharp increase in this value observed upon addition of DTBP to the cumyl chloride—BCl_3—IB polymerizing system,[18] which was explained by the proton abstraction from the growing carbocation by the proton trap. The reasons for this dissimilarity are unknown, but the noticeable deviation of the data obtained by Guhaniyogi and coworkers[18] from the results of other researchers has been noted by the authors themselves.[5]

The published data and our results show that the behavior of proton traps and ordinary n-electron-donating compounds during cationic polymerization is rather similar.[12] However, in our opinion, neglecting functions of these additives other than the proton trapping (carbocation stabilization and so on) does not allow one to explain some experimental facts considered above. Therefore, it seems expedient to formulate the above-posed question in a somewhat different way, namely: whether the effect of the electron-donating additive on the cationic polymerization is reduced to the trapping of protons or is the range of its action wider? The data we obtained regarding 2,6-DMP make it possible to argue that its role in the cationic polymerization of IB is both the removal of free protons from the system and the effect on the carbocationic active center, determining its ability to participate in various chain-limiting reactions.

Thus, the modification of the acyl halide—$AlBr_3$—IB system by the addition of 2,6-DMP makes it possible to obtain PIB with a narrower MWD and a controlled content of the end functional groups both in polar and nonpolar media.

References

1. 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.)].
2. 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.)].
3. M. Sawamoto, *Prog. Polym. Sci.*, 1991, **16**, 111.
4. J. P. Kennedy and R. T. Chou, *J. Macromol. Sci., Chem.*, 1982, **A18**(1), 3.
5. J. P. Kennedy, T. Kelen, S. C. Guhaniyogi, and R. T. Chou, *J. Macromol. Sci., Chem.*, 1982, **A18**(1), 129.
6. F. R. Khalafov, F. M. Nasirov, N. E. Melnikova, B. A. Krentsel, and T. N. Shakhtakhtisky, *Makromol. Chem., Rapid Commun.*, 1985, **6**, 29.
7. A. I. Nesmelov, A. V. Orlinkov, I. S. Akhrem, V. B. Murachev, V. S. Byrikhin, and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1496 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 1352 (Engl. Transl.)].
8. 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.)].
9. V. S. Byrikhin, A. I. Nesmelov, V. B. Murachev, E. A. Ezhova, A. V. Orlinkov, I. S. Akhrem, and M. E. Vol'pin, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 883 [*Russ. Chem. Bull.*, 1993, **42**, 837 (Engl. Transl.)].
10. H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, 1953, **75**, 3865.
11. H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, 1966, **88**, 986.
12. M. Gyor, H.-C. Wang, and R. Faust, *J. Macromol. Sci., Pure Appl. Chem.*, 1992, **A29**(8), 639.
13. G. Kaszas, J. Puskas, C. C. Chen, and J. P. Kennedy, *Polym. Bull.*, 1988, **20**, 413.
14. G. Kaszas, J. Puskas, C. C. Chen, and J. P. Kennedy, *Macromolecules*, 1990, **23**, 3909.
15. G. Kaszas, J. E. Puskas, J. P. Kennedy, and C. C. Chen, *J. Macromol. Sci., Chem.*, 1989, **A26**(8), 1099.
16. D. F. Hoeg, S. Liebman, and L. Schubert, *J. Org. Chem.*, 1963, **28**, 1554.
17. G. Pratap, S. S. Mustafa, and P. Heller, *J. Appl. Polym. Sci.*, 1992, **46**, 559.
18. S. C. Guhaniyogi, J. P. Kennedy, and W. M. Ferry, *J. Macromol. Sci., Chem.*, 1982, **A18**(1), 25.

Received November 20, 1995