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

7.* The criteria for "closeness to the living state" for cationic polymerization of isobutene

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Two criteria for the quantitative estimation of "closeness to the living state" for polymerization systems in which an important role belongs to elimination of a proton from the growing carbocation during cationic polymerization are proposed. The first criterion, $(C=C)_{rel}$, is the proportion of units with C=C bonds in the polymer chains. The second criterion, k_{el}/k_{gr}, is the ratio of the rate constants for proton elimination and chain growth. The criteria are used in experiments on the polymerization of isobutene in hexane and dichloromethane induced by complexes of acyl halides with aluminum bromide. Limitations and fields of application of these criteria are examined.

Key words: isobutene, polyisobutene, molecular weight, end groups; Lewis acids; cationic polymerization.

Previously,[2,3] we have shown that cationic polymerization of isobutene (IB) in *n*-hexane at −78 °C initiated by the acyl complex $MeCOBr \cdot 2\,AlBr_3$ (Ac-2) possesses some features typical of "living" polymerization, namely, a linear increase in the average molecular weight $\bar{M}_n$ as the yield of the polymer increases; invariability of the number of polymeric molecules formed during polymerization; resumption of polymerization accompanied by a further linear increase in $\bar{M}_n$, after the first stage has been completed and a new portion of the monomer has been added. At the same time, analysis of the polymers isolated at various stages of the process made it possible to find out that, as the yield of the polymer increases, the proportion of macromolecules with terminal C=C bonds, inactive in the polymerization, increases and the molecular-weight distribution (MWD) is broadened. The C=C bonds arise through the elimination of protons from growing carbocations rather than through direct chain transfer to the monomer. It was found that the eliminated protons cannot initiate the formation of new polymeric chains under these conditions; therefore, this process is regarded[4] as chain termination, and the rate constants for chain termination and chain growth (k_t and k_{gr}) are determined. The reasons for the absence of initiating activity of protons in the Ac-2 system and in other related systems are considered in detail in the next publication.[5]

It was found[6] that when Ac-2 is replaced by the benzoyl-chloride complex $PhCOCl \cdot 2AlBr_3$ (Bn-2), the probability of the elimination of a proton from the growing center under similar conditions decreases, accompanied by narrowing of the MWD. The addition of 2,6-dimethylpyridine (2,6-DMP) causes a similar effect.[1] The tendency of polyisobutenyl carbocations to eliminate protons, *i.e*, to form end groups with C=C bonds, was estimated using the degree of functionalization $f_{C=C}$, which was determined from the results of ozonization and gel permeation chromatography.[2] In the polymerization initiated by the Bn-2 complex, as in the case of Ac-2, no direct one-step transfer to the monomer was found, because for all the polyisobutene (PIB) samples obtained, $f_{C=C} \approx 100\%$.[3,6] Comparison of the $f_{C=C}$ and $\bar{M}_w/\bar{M}_n$ values for polymer samples, for which the degrees of conversion Q are close and $\bar{M}_n$ are not very much different made it possible to show that the introduction of 2,6-DMP[1] or replacement of Ac-2 by Bn-2 hampers chain termination and brings these systems closer to "living" systems. However, it is not always possible to obtain samples with close Q and $\bar{M}_n$, when some parameter of the process is varied, in which case, it is difficult to evaluate the role of this parameter in bringing the system closer to a "living" system. For example, as the degree of conversion in the polymerization of IB initiated by Ac-2 increases from 28 to 98%, $\bar{M}_n$ increases from 44800 to 157400, $f_{C=C}$ grows from 4.1 to 31%, and $\bar{M}_w/\bar{M}_n$ changes from 1.62 to 3.09.[3]

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*For part 6, see Ref. 1

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Therefore, it seems desirable to use more versatile quantitative criteria for the estimation of the degree to which the system approaches the "living" state, which would allow more objective evaluation of the role of a particular factor. In the present study, we propose two criteria for this purpose.

Previously,[7] seven criteria, compliance with which would allow one to classify a polymerization system as a living system, have been proposed. However, not "truly living" systems but rather those approaching the living state may be of substantial interest from the practical viewpoint, for example, for preparing block copolymers.

Experimental

The procedures for purification and drying of the reagents and solvents (*n*-hexane and dichloromethane), for the preparation of the initiating complexes, for conduction of polymerization in all-sealed glass vacuum setups, for the isolation and analysis of the polymers, and for the calculation of the degree of functionalization have been described previously.[1—4,6,8]

Results and Discussion

The first of the criteria proposed is the $(C{=}C)_{rel}$ value, *i.e.*, the proportion of units with C=C bonds in the overall number of units incorporated in the polymer molecules. As noted above, units with C=C bonds are end units of the PIB chains resulting from elimination of protons:

$$\mathrm{PIB{-}CH_2{-}CMe_2{}^+A^-} \xrightarrow{k_{el}}$$
$$\longrightarrow \mathrm{PIB{-}CH_2{-}C({=}CH_2)Me + H^+A^-},$$

where k_{el} is the rate constant for proton elimination and A^- is the counter-anion.

If the degree of conversion Q is expressed in percent, the overall concentration of macromolecules $[N]$ is determined from the equation

$$[N] = [M]_0 \cdot Q/(\overline{DP}_n \cdot 100), \qquad (1)$$

where $[M]_0$ is the initial concentration of the monomer, $\overline{DP}_n$ is the number-average degree of polymerization (for PIB, $\overline{DP}_n = \overline{M}_n/56$, where 56 is the molecular weight of IB). By definition, $f_{C=C}$ (in %) $= 100 \cdot [N_{C=C}]/[N]$, where $[N_{C=C}]$ is the concentration of macromolecules with end C=C bonds, *i.e.*,

$$[N_{C=C}] = [N] \cdot f_{C=C}/100 = [M]_0 \cdot Q \cdot f_{C=C}/(\overline{DP}_n \cdot 10^4). \qquad (2)$$

This makes it possible to easily obtain the required relation:

$$(C{=}C)_{rel}\ (\text{in }\%) = [N_{C=C}] \cdot 100/([N] \cdot \overline{DP}_n) =$$
$$= f_{C=C}/\overline{DP}_n. \qquad (3)$$

For "truly living" systems, this quantity must be equal to zero, but it increases as the contribution of proton elimination to the process increases. Actually, the $(C{=}C)_{rel}$ value makes it possible to estimate the ratio of the time-averaged probabilities of the competing processes, *viz.*, proton elimination and chain growth (the $f_{C=C}$ values by themselves do not allow this estimation for polymers with different molecular weights). However, $(C{=}C)_{rel}$ characterizes a particular polymeric sample rather than the process. In fact, in systems involving, for example Ac-2 [2—4] and Bn-2,[6] the competing reactions of proton elimination and chain growth have dissimilar orders with respect to the monomer; therefore, the ratio of their probabilities expressed as $(C{=}C)_{rel}$ should change following an increase in the degree of conversion and should depend on the initial monomer concentration. For these reasons, it is more desirable to use the ratio of the rate constants for proton elimination and chain growth k_{el}/k_{gr} as a criterion for the "closeness of a polymerization system to the living state."

In the systems initiated by $\mathrm{RCOX \cdot 2AlBr_3}$ complexes, for example, Ac-2 and Bn-2, the rate of accumulation of end units with C=C bonds resulting from momomolecular proton elimination can be expressed by the following equation:

$$d[N_{C=C}]/dt = k_{el} \cdot [n^*], \qquad (4)$$

where t is time and $[n^*]$ is the concentration of active centers. If we neglect the very small consumption of units with C—C single bonds, the rate of their accumulation in the backbone due to proton elimination can be taken as being equal to the rate of polymerization:

$$-d[M]/dt = k_{gr} \cdot [n^*] \cdot [M], \qquad (5)$$

where [M] is the current concentration of the monomer. By dividing Eq. (4) by Eq. (5), after corresponding permutations, we obtain

$$d[N_{C=C}] = (-d[M]/[M]) \cdot k_{el}/k_{gr}. \qquad (6)$$

Integration and replacement of $\ln([M]_0/[M])$ by $\ln[100/(100 - Q)]$ yields the simple relation:

$$[N_{C=C}] = \ln[100/(100 - Q)] \cdot k_{el}/k_{gr}. \qquad (7)$$

The left sides of Eqs. (2) and (7) are equal; therefore,

$$k_{el}/k_{gr} = \frac{f_{C=C}}{\overline{DP}_n} \cdot \frac{[M]_0}{10^4} \cdot \frac{Q}{\ln[100/(100-Q)]} =$$
$$= (C{=}C)_{rel} \frac{[M]_0}{10^4} \cdot \frac{Q}{\ln[100/(100-Q)]}. \qquad (8)$$

Thus, unlike $(C{=}C)_{rel}$, the second criterion makes it possible to take into account the initial concentration of the monomer and the degree of its conversion, *i.e.*, to compare various polymerization processes based on the analysis of samples obtained under different initial conditions and at different degrees of conversion.

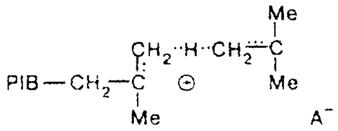
The question arises of whether the second criterion is applicable to other systems, for example, to those initiated by the protonogenic complex $MeCOBr \cdot AlBr_3$ (Ac-1)[2] or to processes carried out in more polar dichloromethane.[8] The answer is "yes" in the case where the contribution of the direct transfer to the monomer:

$$PIB—CH_2—CMe_2{}^{+}A^{-} + M \xrightarrow{k_{tr.M}}$$
$$\longrightarrow PIB—CH_2—C(=CH_2)Me + HM^{+}A^{-},$$

which also yields C=C bonds in polymer chains, is relatively low.

Apparently, for the processes carried out in hexane at a low temperature (−78 °C), there are no grounds to believe that the absence of direct transfer to the monomer is due to some specific feature of the initiator. For the system with Ac-1, this problem is discussed in more detail in one of our papers.[9] However, it is possible that the contribution of this transfer would become quite noticeable if the temperature were substantially increased.

A more polar solvent, dichloromethane, should be even less favorable for the transition state for the direct transfer to the monomer than nonpolar hexane, because this state corresponds to more pronounced charge delocalization than the initial state and, as a consequence, to a substantial decrease in the energy of solvation.[10]



Yet another problem that arises in the evaluation of the legitimacy of using the $(C=C)_{rel}$ and k_{el}/k_{gr} values as criteria of "closeness to the living state" is associated with the role and type of possible chain termination reactions (other than that considered above). In systems initiated by acyl complexes $RCOX \cdot 2AlBr_3$, chain termination due to halogenation of the carbocation (collapse of the ion pair)

$$[PIB—CH_2—CMe_2]^{+}[Al_2Br_6X]^{-} \rightleftharpoons$$
$$\rightleftharpoons PIB—CH_2—CMe_2X \cdot Al_2Br_6$$
$$\text{or } PIB—CH_2—CMe_2Br \cdot Al_2Br_5X$$

is reversible and, furthermore, the equilibrium of this reaction is markedly shifted to the right, *i.e.*, to the "sleeping" form.[3,4,6] In fact, it is practically impossible to imagine the existence of polyisobutenyl cations that grow slowly in nonpolar hexane over a very long polymerization period (several tens of minutes); this kind of stability in carbocations can be ensured only in superacid media (see, for example, the review[11]). Evidently, no irreversible termination occurs in this case. Thus, for the systems under consideration, approach to "living systems with reversible chain termination," according to the classification proposed by Quirk and Lee[7], can be considered, and the criteria that we suggest quite suffice for their characterization.

Table 1. The application of the criteria for the "closeness to the living state" to the polymerization of IB under the action of acetyl complexes Ac-2 and Ac-1 (hexane, −78 °C, $[IB]_0$ = 1.25 mol L^{-1})*

Entry	Q (%)	$\bar{M}_n \cdot 10^{-3}$	$f_{C=C}$ (%)	$(C=C)_{rel}$ (%)	$(C=C)_{rel}$ (arb.u.)	k_{el}/k_{gr} /mol L^{-1}	k_{el}/k_{gr} (arb.u.)
A-2 as the initiator, [MeCOBr] = 4.1 mmol L^{-1}							
1	28	44.8	4.1	$5.1 \cdot 10^{-3}$	61	$5.5 \cdot 10^{-5}$	98
2	53	96.8	11.4	$6.6 \cdot 10^{-3}$	79	$5.8 \cdot 10^{-5}$	104
3	76	126.0	19.0	$8.4 \cdot 10^{-3}$	100	$5.6 \cdot 10^{-5}$	100
4	87	132.8	27.5	$11.6 \cdot 10^{-3}$	138	$6.2 \cdot 10^{-5}$	111
5	94	151.0	26.0	$9.6 \cdot 10^{-3}$	114	$4.0 \cdot 10^{-5}$	71
6	98	157.4	31.0	$11.0 \cdot 10^{-3}$	131	$3.5 \cdot 10^{-5}$	62
				Average		$5.1 \cdot 10^{-5}$	
Ac-1 as the initiator, [MeCOBr] = 9.7 mmol L^{-1}							
7	22	138.7	29.4	$11.9 \cdot 10^{-3}$	141	$13.2 \cdot 10^{-5}$	236
8	69	119.4	36.7	$17.2 \cdot 10^{-3}$	204	$12.8 \cdot 10^{-5}$	229
9	96	106.5	41.4	$21.8 \cdot 10^{-3}$	260	$8.1 \cdot 10^{-5}$	145
				Average		$11.2 \cdot 10^{-5}$	

* Experimental data were taken from Ref. 2.

When the initiator Ac-1 in hexane is used, the $\bar{M}_n$ values decrease somewhat as the degree of conversion increases (Table 1), and the efficiency of initiation[3] and $f_{C=C}$ (see Table 1) increase. One of the peculiar features of the polymerization of IB in the system containing Ac-1 is the occurrence of irreversible chain termination through the collapse of ion pairs.[9] In this case, the criteria in question can serve for the estimation of the relative contribution of proton elimination to the overall process of restriction of chain growth.

Generally, the k_{el}/k_{gr} value is a better criterion than $(C=C)_{rel}$ for evaluating the role of processes affording terminal units with C=C bonds that are inactive in polymerization in nonpolar (hexane) and moderately polar (dichloromethane) media at low temperatures, because in the former case, there is no need to compare only those samples with close $[M]_0$ and Q. On passing to higher temperatures, one must make sure that proton elimination retains its predominant role in the formation of end C=C bonds. If this is not the case, and direct transfer to the monomer becomes more significant, the first criterion must be used. It is easy to show that, in this case, regardless of the degree of conversion and the initial concentration of the monomer, the relation has the following form:

$$k_{tr.M}/k_{gr} = f_{C=C}/(\bar{DP}_n \cdot 100) = (C=C)_{rel}/100.$$

At Q = 100%, Eq. (8) cannot be solved analytically; as Q approaches this value, the relative error of the calculation of k_{el}/k_{gr} sharply decreases due to inaccuracy of the experiment. Subsequently, in the calculations of k_{el}/k_{gr} for samples obtained formally at 100% degree of conversion (the data of dilatometry), we set Q = 99%. Using this assumption, the possible error can be found by comparing the $Q/\ln[100/(100 - Q)]$ values at Q

Table 2. Evaluation of the viability of polymerization systems based on the criteria proposed (−78 °C)

Entry	Initiator (C/mmol L^{-1})	Solvent (additive, C/mmol L^{-1})	$[\mathrm{IB}]_0$ /mol L^{-1}	Q (%)	$\bar{M}_n \cdot 10^{-3}$	$f_{C=C}$ (%)	$(C=C)_{rel}$		k_{el}/k_{gr}	
							(%)	(arb. u.)	/mol L^{-1}	(arb. u.)
10	Ac-1 (7.50)	*n*-Hexane	1.64	79	108	46	$2.4 \cdot 10^{-2}$	285	$2.0 \cdot 10^{-4}$	355
11	Ac-1 (8.55)	Dichloromethane	0.80	100	7.1	31	$2.4 \cdot 10^{-1}$	2900	$4.2 \cdot 10^{-4}$	750
12	Ac-2 (8.55)	Dichloromethane	0.80	100	5.2	27	$2.9 \cdot 10^{-1}$	346	$5.0 \cdot 10^{-4}$	900
13	Ac-1 (6.40)	Dichloromethane (2,6-DMP, 1.1)	0.99	20	16.4	19	$6.5 \cdot 10^{-2}$	775	$5.8 \cdot 10^{-4}$	1020
14	Ac-2 (6.40)	Dichloromethane (2,6-DMP, 1.1)	0.99	93	25.2	11	$2.4 \cdot 10^{-2}$	290	$8.5 \cdot 10^{-5}$	155
15	Ac-2 (4.10)	*n*-Hexane (2,6-DMP, 0.5)	1.25	42	86.9	1	$6.4 \cdot 10^{-4}$	8	$6.2 \cdot 10^{-6}$	11
16	Ac-2 (4.10)	*n*-Hexane (2,6-DMP, 0.5)	1.25	99	208	9	$2.4 \cdot 10^{-3}$	29	$6.6 \cdot 10^{-6}$	12
17	Bn-2 (4.60)	*n*-Hexane	1.02	84	337	3	$5.0 \cdot 10^{-4}$	6	$2.3 \cdot 10^{-6}$	4
18	Bn-2 (7.50)	*n*-Hexane	2.35	82	252	3	$6.7 \cdot 10^{-4}$	8	$7.5 \cdot 10^{-6}$	13

close to 100%: 25.1 at 98%, 21.7 at 99%, 18.8 at 99.5%, and 16.6 at 99.9%.

To illustrate the applicability of the criteria in question, let us consider some data reported in our previous studies and some data not published before. For convenience, in addition to the absolute values for $(C=C)_{rel}$ and k_{el}/k_{gr} calculated from Eqs. (3) and (8), we have expressed these values in arbitrary units (arb.u.) by taking both parameters for entry *3* in Table 1 as being equal to 100. The k_{el}/k_{gr} calculated for this entry is nearly equal to the k_{el}/k_{gr} ratio calculated previously[4] from the corresponding magnitudes of rate constants for polymerization of IB under these conditions in the presence of Ac-2.

From the results of calculations for the polymerization of IB initiated by Ac-2 and Ac-1 listed in Table 1, it can be seen that $(C=C)_{rel}$ increases as the degree of conversion increases, while the k_{el}/k_{gr} ratio remains virtually constant up to a high degree of conversion (~90%); this confirms the mechanism suggested for the appearance of C=C double bonds in the polymer chains, *viz.*, monomolecular proton elimination. The decrease in k_{el}/k_{gr} at the end of the process may be partly due to the increase in the relative error of calculations at high degrees of conversion. However, this decrease is still quite substantial and is observed for both systems. This suggests that it is a regular feature rather than an artifact.

Let us consider the use of the first and second criteria for other samples obtained in hexane or dichloromethane (Table 2). The systems in dichloromethane are less "living" than those in hexane (*cf.* entries *10* and *11*, *6* and *12*), which is especially clearly manifested in the presence of the initiating complex Ac-2. This decrease in "viability" on going to a more polar solvent has been also observed in the polymerization of *cis*-, *trans*-ethylpropenyl ethers in the presence of HI/I_2.[12] The addition of 2,6-DMP ensures an increase in the "viability" (decrease in k_{el}/k_{gr}) for the combinations Ac-2/hexane (*cf.* entries *1*—*6* and *15*, *16*) and Ac-2/dichloromethane (*cf.* entries *12* and *14*), but not for Ac-1/dichloromethane (*cf.* entries *11* and *13*). It is quite probable that in the latter case, a large portion of 2,6-DMP is spent for trapping protons, and is thus unable to stabilize carbocations.[1] A "viability" similar to that observed on the addition of 2,6-DMP to the Ac-2/hexane system is achieved when polymerization is initiated by Bn-2 in hexane (*cf.* entries *15*, *16* and *17* and *18*). The low tendency of the growing centers to eliminate protons in systems initiated by the Bn-2 complex has been discussed previously.[6]

Thus, the criteria for "closeness to the living state" that we propose make it possible to estimate quantitatively the degree to which a particular system has approached the "living" state and to demonstrate the efficiency of various characteristics of the system in suppressing proton elimination and/or chain transfer. Apparently, these criteria can also be used in relation to polymerization processes involving other monomers and initiators. In this connection, based on the analysis of Eqs. (3) and (8) and using the data obtained and the remarks made above, we can give some recommendations on using the first and second criteria depending on the ratio of the contributions of various processes to chain restriction.

1. Chain termination does not occur or is reversible. The reversibility of chain termination means that during polymerization, the growing centers are able to be transformed repeatedly from the covalently bound "sleeping" forms into active ionic forms and back.[13] Several variants are possible.

a. Elimination of a proton (monomolecular process) resulting in chain termination (as in the systems with Ac-2, Bn-2, *etc.*) or to chain transfer, due to the subsequent participation of the proton in initiation, is the main reaction restricting chain growth. In this case, it is more expedient to use the second criterion, k_{el}/k_{gr}, more preferably, when the degree of conversion is no more than 90%. When the formal degree of conversion is 100%, a different Q value close to it, for example, 99%, should be used in the calculations.

b. Direct transfer to the monomer (bimolecular process) predominates. In this case, the first criterion, $(C{=}C)_{rel}$, should be used.

c. Both types of reactions mentioned above make comparable contributions to the chain restriction. The "viability" of the system should be estimated by comparing $(C{=}C)_{rel}$ values at close $[M]_0$ and Q.

d. The mechanism by which the end C=C bonds are formed is unknown. As in the former case, it is expedient to compare $(C{=}C)_{rel}$ at close $[M]_0$ and Q. If it is possible to withdraw samples during the process and to analyze them thereafter, our criteria make it possible to elucidate the unknown mechanism: $(C{=}C)_{rel}$ remains unchanged as the degree of conversion increases for type 1(*b*) systems, while k_{el}/k_{gr} is constant for type 1(*a*) systems (at $Q < 90\%$).

e. The material chains are mostly restricted through transfer to the solvent (pseudo-monomolecular reaction). In this case, the recommendations given in 1(*a*) can be used, but the results of the analysis of the polymers for solvent fragments are needed for the calculations.

2. In addition to reactions leading to the formation of the end C=C bonds or to chain transfer to the solvent, other reactions corresponding to irreversible chain termination occur in the system, and the contributions of both processes to the restriction of material chains are comparable. For these systems, the same cases (*a—e*) as for the systems without chain termination or with reversible termination can be distinguished. Hence, the same recommendations should be applied to each of these cases. In this case, "closeness to the living state" estimated using the above criteria is possible only up to the level allowed by irreversible termination. This situation occurred in the analysis of polymerization of IB in hexane under the action of Ac-1 complexes.[9] In this case, it was proposed to characterize the contribution of irreversible termination by the ratio between the rate constants of chain termination and chain growth, k_t/k_{gr}, calculated by a procedure reported previously.[9]

3. The main role in chain restriction belongs to the irreversible termination. In this case, the use of the criteria represented by Eqs. (3) and (8) makes no sense, and the "closeness to the living state" should be evaluated using the k_t/k_{gr} value.[9]

The use of our criteria in relation to inifer type systems[14] can be expedient only for estimation of the efficiency of inifers.

In conclusion, let us note that the criteria under consideration can also be used for other chain polymerization processes.

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