Macromol. Symp. **2004**, *215*, 281-293

Dual Reactivity of Magnesium Compounds as Initiators for Anionic and Cationic Polymerization

Alexander Arest-Yakubovich,[1] Boris Nakhmanovich,[1] Irina Zolotareva,[1] Alexander Yakimansky,[2] Natalia Pakuro[1]*

[1]Karpov Institute of Physical Chemistry, 10 Vorontsovo pole, Moscow 105064, Russia
E-mail: arest@cc.nifhi.ac.ru
[2]Institute of Macromolecular Compounds, 31 Bolshoi Prospect V.O., St. Petersburg 199004, Russia

Summary: Organomagnesium compounds are well known initiators of anionic polymerization of polar monomers. However, we have found recently that in the presence of compounds with labile halogen atoms, e.g., benzyl chloride, they are also active initiators of cationic polymerization of isobutylene and styrene in hydrocarbon media. The tentative scheme of cationic initiation is suggested assuming the formation of benzyl cation connected with $Mg_2Cl_5^-$ counter-ion. The scheme is confirmed by quantum-chemical calculations and ^1H NMR analysis of polyisobutylene. On addition of a polar monomer, *N,N*-dimethylacrylamide or 2-vinylpyridine, to Bu_2Mg-BzCl-isobutylene polymerizing mixture, the former readily polymerizes. The mixture of homopolymers rather than block copolymers is formed in this case, however, this fact proves the co-existence of anionic and cationic centers in the system.

Keywords: anionic polymerization; cationic polymerization; initiators; isobutylene; magnesium compounds

Introduction

Magnesium is typical of electropositive metals, i.e. metals with the lowest electron affinity. According to the Pauling's scale, its electronegativity is 1.2 and is close to that of lithium (1.0) and potassium (1.0).[1] According to Schlosser,[2] organomagnesium compounds, along with compounds of other alkali and alkaline earth metals are considered as "polar organometallics". Similar to other metals of these groups, in the presence of electron donor solvents magnesium relatively easily transforms into a cation, donating its electrons to strong electron acceptors, for example, to condensed aromatic hydrocarbons.[3, 4] The capability of alkylmagnesiums to initiate anionic polymerization of such monomers as (meth)acrylic esters, 2- and 4-vinylpyridine, *N,N*-

DOI: 10.1002/masy.200451122

dimethyl and diethylacrylamides is well known.[5-8]

More surprising is that, contrary to all other alkali and alkaline earth metals, under certain conditions magnesium is able to participate in reactions of the cationic type. In the course of recent studies we have found that in the presence of compounds with labile halogen atom, organomagnesium compounds initiate polymerization of isobutylene, styrene, *p*-chloromethylstyrene (*p*-CMS), and their comonomer mixtures. The most convincing evidence of the cationic nature of the process is the polymerization of isobutylene, which proceeds homogeneously in aliphatic or aromatic hydrocarbons, at room temperature, the quantitative yield being reached in a few minutes.

To our knowledge, in the past the possibility for magnesium to participate in cationic processes has been reported only twice, both in 60s. Bryce-Smith et al., who succeeded in the synthesis of etherless Grignard compounds, found that the products obtained with an excess of alkylhalogenides and in the medium of aromatic hydrocarbons catalysed the Friedel-Crafts alkylation of the latter.[9, 10] Somewhat later, another group reported that finely divided $MgCl_2$ initiated polymerization of isobutylene.[11] In contrast to the present study, in both of these cases reactions proceeded heterogeneously, and the mechanism was suggested to involve electron-deficient structures on the surface of deformed crystals. These works performed about 40 years ago, apparently were not extended.

In the present paper, along with new data on anionic polymerization of *N,N*-dialkylacrylamides, the results of our recent investigations on homogeneous cationic polymerization in the presence of magnesium compounds are given in detail, and the possible mechanism of initiation of this process is discussed. In addition, the results of quantum chemical calculations are given confirming the possibility of formation of active centers, where magnesium is incorporated into a negative counter-ion, and a probable structure of such counter-ion is proposed.

Experimental

All operations were carried out under high vacuum in an all-glass apparatus using break-seal techniques. The general procedures for reagent purification and polymerization were described earlier.[8, 12, 13] Dibutylmagnesium, Bu_2Mg, (Aldrich) was used as received. Benzyl chloride, BzCl, (Aldrich) was repeatedly dried with calcium hydride and distilled under vacuum into ampoules with break-seals.

Molecular weights and molecular weight distributions of the polymers were measured by size exclusion chromatography (SEC) with a Waters-200 instrument equipped with RI and UV (264 nm) detectors. THF was used as an eluent. Polybutadiene calibration was used for polyisobutylene.

The ^{1}H NMR spectra were obtained with 5% CCl_4 solution at 30 °C using a Gemini-300 (Varian) spectrometer operating at 300 MHz. Chemical shifts in ppm were referenced to hexamethyldisiloxane internal standard.

All Density Functional Theory (DFT) geometry optimizations were performed using the TURBOMOLE quantum chemical program[14] with the BP86 gradient corrected functional and split valence basis set with polarization functions at non-hydrogen atoms (SVP) of 6-31G* quality. All computational details have been published elsewhere.[15]

For the optimized geometries, non-specific solvation energies of all the studied structures were calculated semi-empirically using solvent continuum model [16] implemented into the modified MOPAC 6.0 program. PM-3 parametrization was used. The solvent polarity was characterized by its dielectric constant, ε.

Anionic Polymerization

Organomagnesium compounds are incapable of initiating polymerization of non-polar monomers in the absence of strong solvating agents.[3, 5] However, they readily initiate polymerization of (meth)acrylic esters and other monomers containing polar groups.[5, 6] In particular, it was shown recently that organomagnesium compounds are very reactive in the polymerization of *N,N*-dialkyl acrylamides.[7, 8] Generally speaking, anionic polymerization of *N,N*-dimethylacrylamide (DMA) was reported for the first time many years ago.[17] However, the polymer synthesized in the first works performed with lithium initiator, was partially crystalline and water-insoluble and had not attracted much attention. Only recently it was found that other initiators yield water-soluble polymers, which generated a new interest in anionic polymerization of such monomers.[18] During last few years, we studied polymerization of DMA and *N,N*-diethylacrylamide (DEA) under the action of a number of derivatives of alkaline earth metals including magnesium.[8] Some results of this study are interesting from the viewpoint of general theory of stereoregulation in anionic polymerization.

Data on the stereostructure of PDMA and PDEA obtained with organomagnesium initiators are shown in Table 1. For comparison, the results obtained with compounds of lithium and some other metals are also included.

Table 1. Structure of PDMA and PDEA formed with various anionic initiators at -50 °C

Run No.	Monomer	Initiator	Solvent	Triad content		
				mm	*mr*	*rr*
1	DMA	BuLi	Toluene	53	47[a)]	
2	DMA	Bu_2Mg	THF	24	76[a)]	
3	DMA	Bu_2Mg	Toluene	29	71[a)]	
4	DMA	Tr_2Ba[b)]	Toluene	60	40[a)]	
5	DEA	DPHLi[c)]	THF	55	41	4
6	DEA	Bu_2Mg	THF	10	87	3
7	DEA	EtMgBr	THF	28	66	6
8	DEA	Tr_2Ba[b)]	THF	20	77	3

[a)] Sum of *mr* and *rr* configurations
[b)] Bis(triphenylmethyl)barium
[c)] 1,1-Diphenylhexyllithium

The analysis of the data obtained with these little studied monomers shows several deviations from common rules of stereoregulation established earlier, mainly for poly(acrylic esters). Thus, it is admitted that magnesium, similar to lithium, due to its small ionic radius has to favor the formation of polymers with high content of isotactic structure.[6] As can be seen from Table 1, lithium, indeed, forms predominantly isotactic structure with both monomers whereas magnesium compounds give rise to hetero- and syndiotactic polymers. (For PDMA, unfortunately, quantitative determination of *mr* and *rr* triad content is hardly possible due to superposition of peaks in the NMR-spectra.) A low content of isotactic structure in PDEA obtained with magnesium was reported also by Kobayashi et al.[7]

Further, it was shown recently that the isotactic structure content in PDMA's obtained with various alkali metals monotonously decreases with increasing ionic radius of counter-ion from ~ 55 % with lithium to 3 % with Cs.[18] On the contrary, as is seen from Table 1, in the case of alkaline earth metals, the stereospecificity in the formation of iso-structure of PDMA increases with increasing ionic radius, so that the polymer obtained in the presence of counter-ion with the largest radius, barium, is similar, with respect to its structure and some other properties, to the lithium-initiated polymer.[8] On the other hand, in the case of DEA, the compounds of magnesium and barium give polymers of approximately the same structure, thus, the counter-ion size only slightly affects the polymer structure.

The reasons for such sharp difference between alkali and alkaline earth metals with respect to stereoregulation in DMA polymerization, as well as for the difference in the behavior of DMA and DEA with respect to alkaline earth initiators are still not clear.

Cationic polymerization

In the course of recent studies we found that, in the presence of compounds with labile halogen atom such as benzyl chloride (BzCl) or *p*-chloromethylstyrene (*p*-CMS), magnesium compounds also readily initiate cationic polymerization. The most convincing evidence is the polymerization of isobutylene, which is known to polymerize only cationically. Typical experimental results on isobutylene polymerization in hydrocarbon solvents are shown in Table 2. In standard experiments (runs 9-12), solvent is condensed from the vacuum line into the ampoule, after that solutions of Bu_2Mg and chlorine-containing component are introduced. The ampoule is frozen and the monomer is condensed there under vacuum. Then the mixture is melted, shaken vigorously and heated up to room temperature. During 10 to 15 min the pale yellow solution formed shows no signs of reaction, after that an intensive heat evolution is observed and the reaction is completed in a few minutes. At molar ratio $RCl:Bu_2Mg \geq 4:1$, the polymerization proceeds with the quantitative yield, at lower ratios (run 9), a similar qualitative pattern is observed, but heat evolution is less and the monomer conversion is not complete.

The polymers obtained at room temperature have low M_n and a broad MWD, which is explained by intensive chain transfer. Nevertheless, irreversible chain termination of active centers is not very important, and the system remains active for sufficiently long time. For example, in one experiment the second monomer, styrene, was introduced 30 min after isobutylene polymerization was finished and it also was quickly polymerized quantitatively. However, the overall molecular weight did not increase as could be expected at intensive chain transfer.

At -50 °C the polymerization is much slower and high monomer conversion is reached only after several hours (runs 13, 14). In this respect the process differs considerably from most other cationic polymerizations of isobutylene where the polymerization rate increases with decreasing temperature.[19-21] However, now it is difficult to judge whether this retardation is related to slower formation of initiating complex or to the decrease in the propagation rate constant.

Table 2. Isobutylene polymerization initiated by Bu_2Mg mixtures with halogen-containing compounds. $[Bu_2Mg] = 1 \cdot 10^{-2}$ mol·L^{-1}; $[IB]_0 = 5$ mol·L^{-1}

Run No.	Solvent	Additive	Cl:Mg molar ratio	T °C	Polymer yield %	$M_n \cdot 10^{-3}$	M_w/M_n
9	Toluene	BzCl	2:1	r.t.[a)]	25[b)]	-	-
10	Heptane	BzCl	4:1	r.t.[a)]	88[b)]	1.4	7.7
11	Toluene	BzCl	6:1	r.t.[a)]	92[b)]	-	-
12	Toluene	BzCl	16:1	r.t.[a)]	90[b)]	1.1	11
13	Heptane	BzCl	4:1	-50	90[c)]	6.2	15
14	Toluene	*p*-CMS[d)]	22:1	-50	84[c)]	0.7	8.5

[a)] room temperature
[b)] Polymerization time – several minutes (see text)
[c)] Polymerization time - 4 hours
[d)] *p*-Chloromethylstyrene

Besides BzCl, *p*-CMS can be also used as an initiating component. This substance is known to be an inimer in cationic self-condensing vinyl polymerization resulting in the formation of hyperbranched polymers (see paper[22] and references therein). The polymer obtained in copolymerization of isobutylene with a small amount of *p*-CMS (run 14, [*p*-CMS]:[IB] = 0.09) had much lower apparent molecular weight in comparison to isobutylene homopolymer, obtained under the same conditions (run 13). This fact gives evidence to the formation of highly branched polymer.

Figure 1 shows ^1H NMR spectra of polymers formed in heptane at different temperatures. The spectrum of the polymer obtained at room temperature (line 1) contains signals at 4.62; 4.85, and 5.15 ppm, which are attributed to terminal double bonds[19], whereas in the spectrum of the polymer formed at -50 °C (line 2) these peaks are absent. This agreed well with M_n values given in Table 2 indicating intensive chain transfer in the former case and its suppression in the latter. In addition, the ^1H NMR-spectra contain signals at 1.98 ppm ascribed to the protons of methylene group of the terminal $-CH_2-C(CH_3)_2-Cl$ unit[19], as well as signals of aromatic protons near 7.2 ppm. IR spectra of the polymers also contain characteristic bands of aromatic rings (697 and 745 cm^{-1}). The presence of the latter in the polymer formed in heptane may be explained only by the participation of benzyl group of halogen-containing component in initiation. This topic is discussed in more detail in the next section.

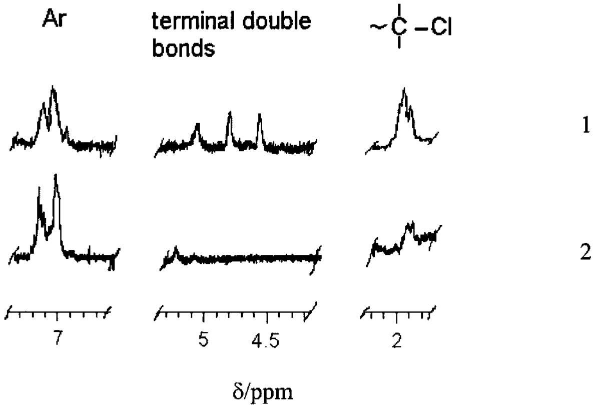

Figure 1. ^{1}H NMR-spectra of polyisobutylene obtained in heptane at room temperature (1) and at -50 °C (2)

Similarly, the Bu$_2$Mg - BzCl mixture initiates polymerization of styrene which cannot be polymerized by organomagnesium compounds in hydrocarbon media. Corresponding data are given in Table 3. At sufficient excess BzCl (run 17), styrene polymerization proceeds similar to isobutylene polymerization: after 10 - 15 min induction period a vigorous reaction starts accompanied with a marked heat evolution. In another experiment (run 18), styrene was added to the Bu$_2$Mg - BzCl mixture in toluene, aged for 20 h at room temperature. In this case, polymerization started immediately after the monomer addition. This confirmed that the induction period is related to the formation of cationic active centers.

The UV-spectum obtained ca. 10 min after completion of styrene polymerization has distinct absorbance maximum at ca. 420 nm. As is known now, this maximum does not correspond to instable polystyrene carbenium ions themselves but to the cyclic products of their secondary transformations.[23,24] Nevertheless, the presence of the maximum confirms cationic character of the processes.

Table 3. Styrene polymerization initiated by Bu_2Mg mixtures with halogen-containing compounds. Toluene, 30 °C. $[Bu_2Mg] = 1 \cdot 10^{-2}$ mol·L^{-1}; $[St]_0 = 2.5$ mol·L^{-1}

Run No.	Additive	Cl:Mg molar ratio	Polymer yield %	$M_n \cdot 10^{-3}$	M_w/M_n
15	BzCl	1:1	21	1.3	2.0
16	BzCl	2:1	25	1.7	2.0
17	BzCl	14:1	100	0.6	2.5
18[a)]	BzCl	14:1	92	0.8	4.0
19	*p*-CMS[b)]	70:1	84	1.5	65

[a)] Toluene solution of Bu_2Mg +BzCl was aged for 20 hours at room temperature prior to addition of styrene

[b)] *p*-Chloromethylstyrene; [St]:[*p*CMS] = 2.8:1

In the presence of Bu_2Mg, styrene also readily copolymerizes with *p*-CMS. In this case (run 19, [St]:[*p*-CMS] = 2.8:1), a vigorous polymerization starts without any marked induction period. The polymer obtained has a very broad MWD and is well soluble in THF in spite of high values of $M_w = 94 \cdot 10^3$ and, especially, $M_z = 2.6 \cdot 10^6$. This fact allows to suppose a highly branched structure of the polymer, similar to the case of isobutylene – *p*-CMS copolymerization.

Tentative scheme of cationic initiation

The whole complex of data presented leaves no doubts that polymerizations of isobutylene and styrene in the presence of Bu_2Mg mixture with labile halogen-containing compounds, in particular, BzCl, proceed via cationic mechanism. The presence of aromatic fragments in polyisobutylene macromolecule as detected by NMR- and IR-spectroscopy, proves the participation of benzyl cation in the initiation. In such a case, magnesium obviously should be incorporated into a negative counter-ion. Therefore, the possible scheme of the generation of cationic active sites should include two main steps: (i) the formation of magnesium halogenides as a result of the exchange between organomagnesium and halogen-containing components, and (ii) the interaction of magnesium halogenides formed with excess BzCl leading to the formation of cationogenic complexes.

The existence of the first step does not need special proofs because reactions of such type are characteristic of organometallic compounds[2].

The possibility of the second step, however, is not obvious and was not considered earlier. In order to estimate the probability of this reaction, quantum chemical calculations were performed.

Relative stability of various forms of chlorine-containing magnesium anions was calculated. A thermodynamically favourable form of the $Mg_2Cl_5^-$ complex anion with symmetry D_{3h} (Figure 2a) was found. It appeared to be 29.5 kcal/mol more stable than the D_{2d}-form of the anion (Figure 2b), which is explained by the fact that Mg atoms are bound via three bridge Cl atoms in the former and only via one Cl atom in the latter case.

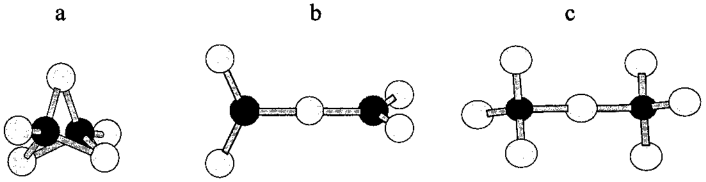

Figure 2. The structures of $Mg_2Cl_5^-$, D_{3h}-symmetry (a), $Mg_2Cl_5^-$, D_{2d}-symmetry (b), $Al_2Cl_7^-$, D_{3d}-symmetry (c) (metal atoms are black, chlorine atoms are gray).

Further, reaction enthalpies of the formation of benzyl cation in the reaction of magnesium chloride with benzyl chloride were calculated both for vacuum (dielectric constant $\varepsilon = 1$) and for toluene medium ($\varepsilon = 2.3$) and compared with enthalpies of similar reactions of such typical cationic catalyst as $AlCl_3$ (Table 4).

Table 4. Calculated reaction enthalpies

Route No	Reaction	Reaction enthalpy, kcal/mol	
		$\varepsilon=1$[a)]	$\varepsilon=2.3$[b)]
1	$AlCl_3 + C_6H_5CH_2Cl \rightarrow AlCl_4^- + C_6H_5CH_2^+$	83.5	32.1
2	$MgCl_2 + C_6H_5CH_2Cl \rightarrow MgCl_3^- + C_6H_5CH_2^+$	95.7	46.9
3	$2AlCl_3 + C_6H_5CH_2Cl \rightarrow Al_2Cl_7^- + C_6H_5CH_2^+$	57.3	14.2
4	$2MgCl_2 + C_6H_5CH_2Cl \rightarrow Mg_2Cl_5^- + C_6H_5CH_2^+$	28.5[c)]	–8.2[c)]
5	$2MgCl_2 + C_6H_5CH_2Cl \rightarrow Mg_2Cl_5^- + C_6H_5CH_2^+$	58.2[d)]	20.5[d)]

[a)] For reactants and products, BP86/SVP total energies are used.

[b)] For reactants and products, sums of BP86/SVP total energies and PM-3 solvation energies are used.

[c)] $Mg_2Cl_5^-$ is in the D_{3h}-form with three bridge Cl atoms between Mg atoms.

[d)] $Mg_2Cl_5^-$ is in the D_{2d}-form with one bridge Cl atom between Mg atoms.

It was found that the ionization of benzyl chloride with the formation of D_{3h}-form of $Mg_2Cl_5^-$ anion (route 4) is energetically possible and even much more favorable than the corresponding reaction of $AlCl_3$ both with the formation of usually assumed $AlCl_4^-$ counter-ion [25] (route 1) and with the formation of more stable $Al_2Cl_7^-$ (route 3) which also contains only one bridge Cl atom (Figure 2c).

Taking into account all said above and the results of calculations, the following scheme of reactions leading to the generation of cationic active centres in the system under consideration may be suggested as a first approximation:

$$Bu_2Mg + BzCl \rightarrow BuMgCl + Bz\text{-}Bu \qquad (1)$$

$$BuMgCl + BzCl \rightarrow MgCl_2 + Bz\text{-}Bu \qquad (2)$$

$$2MgCl_2 + BzCl \rightarrow Mg_2Cl_5^- + Bz^+ \qquad (3)$$

The key point of the Scheme is the binding of $MgCl_2$ formed with the excess BzCl. As a result, magnesium chloride remains in solution and reactions (1)-(3) seem to be of equilibrium character. For example, as is seen from Table 4, in order to obtain a high yield of polyisobutylene one needs 4-fold molar excess of BzCl, whereas according to the stoichiometry of reactions (1)-(3), only 2.5-fold molar excess is necessary for complete binding of Bu_2Mg. It is probable that the equilibrium of the ionization reaction (3) is not completely shifted to the right-hand side. Other considerations concerning the possible reversibility of at least a part of reactions presented by the Scheme will be given in the next section.

An attempt of one-pot synthesis of amphiphilic isobutylene block copolymers

After we have found the ability of magnesium compounds to initiate both anionic and cationic polymerization it seemed attractive to check the possibility of one-pot synthesis of block copolymers of isobutylene with polar monomers. Several test experiments were performed. In all cases, the initiating mixture was BzCl – Bu_2Mg at 4:1 molar ratio, the polymerization temperature -50 °C.

(i) In the first experiment, the DMA – isobutylene mixture (molar ratio ~1:1) was prepared in toluene, then, BzCl was added to the mixture and, after cooling to -50 °C, Bu_2Mg was introduced. Immediately after that the instantaneous polymerization of DMA was observed with precipitation of the polymer. The reaction mixture was allowed to stand for another 4 hours at -50 °C, then the reaction was quenched with methanol and the reaction mixture was washed with heptane, thoroughly separating the extract from the precipitate. According to NMR and IR spectroscopy, the precipitate was pure PDMA at a quantitative yield, and the product isolated from the heptane extract was pure polyisobutylene (yield ca. 20-30 %).

These results may be explained by the fact that due to a high reactivity of DMA[8] it has reacted with Bu_2Mg before the latter had a chance to react with BzCl. Then a slow reaction of unreacted part of Bu_2Mg with BzCl followed resulted in the formation of cationic active centers. Incomplete conversion of isobutylene may be explained by the presence of a large amount of electron donor carbonyl groups which are inhibitors of cationic polymerization.

The next experiments were performed according to another scheme.

(ii) Isobutylene was polymerized in heptane at -50 °C with BzCl – Bu_2Mg mixture. 3 hours after the polymerization started DMA was introduced which was polymerized instantly with the precipitation of the polymer. The mixture was washed with heptane, similar to preceding experiment. Also in this case the precipitate contained pure PDMA (yield 67%), whereas isobutylene homopolymer was isolated from heptane extract (yield ~60%).

(iii) One more experiment was made according to the same scheme. 2-Vinylpyridine (2-VP) was introduced into the system 4 hours after the beginning of isobutylene polymerization. Similar to DMA, 2-VP also polymerized very quickly leading to the formation of partially soluble yellow polymer and yellow-brown precipitate. Ethanol was used for separation of the reaction products in this case, pure polyisobutylene (yield ~80%) being detected by NMR in the precipitate and pure poly-2-VP (yield ~48%) in the ethanol extract.

In two last experiments, the formation of cationic centers initiating isobutylene polymerization obviously took place before the addition of the second monomer. Nevertheless, the system was able to initiate anionic polymerization of polar monomers, i.e. DMA or 2-VP. Probably, due to homogeneity of the system, $MgCl_2$ formed does not precipitate but remains in the solution in the complex-bound state. As a consequence, as was mentioned in the previous section, exchange reactions (1)-(3) are reversible. The equilibrium is not completely shifted to the right hand side so that a part of the compounds with a Mg – C bond, e. g., Bu_2Mg or BuMgCl, remains in the solution and initiates anionic polymerization of polar component, which is terminated shortly thereafter by excess BzCl.

Thus, the attempts to obtain block copolymers via the studied way were unsuccessful. However, the fact of simultaneous proceeding of anionic and cationic polymerization in one and the same system is not trivial and very interesting from scientific point of view.

Conclusion

Therefore, magnesium, apparently, is the only non-transition metal whose compounds are capable of initiating both anionic and cationic polymerization. The possible mechanism of cationic initiation which proceeds in the presence of compounds with labile halogen atoms includes the exchange between organomagnesium and organohalogen components with the subsequent ionization of the latter as a result of their interaction with magnesium halogenides formed. The mechanism is confirmed by the ^{1}H NMR analysis of polyisobutylene obtained in Bu_2Mg-BzCl system. According to the data of quantum-chemical calculations the driving force of ionization is the formation of energetically favorable $Mg_2Cl_5^-$ counter-ion with D_{3h} symmetry where Mg-atoms are bound via three bridge Cl atoms.

A very interesting feature of the Bu_2Mg-BzCl system is co-existence of anionic and cationic centers due to which such different monomers as isobutylene and *N,N*-dimethylacrylamide can be polymerized simultaneously. However, only homopolymer mixture rather than block copolymer is formed in this case.

Acknowledgment

This work was supported by Russian Foundation of Basic Research, project No. 03-03-32930.

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