Synthesis of caprolactamates of Group II metals

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Caprolactamates of alkaline-earth metals and magnesium of the general formula $M[\overline{N-(CH_2)_5-CO}]_2$, where M = Mg, Ca, Sr, and Ba, were synthesized from alkoxides, hydrides, and organometallic compounds of these metals and ε-caprolactam. The catalytic activities of caprolactamates obtained under conditions of anionic polymerization of ε-caprolactam were compared. It was demonstrated that the purest caprolactamates and, hence, the most effective catalysts of anionic polymerization of lactams can be obtained from organometallic and hydride compounds of these metals. The reactivities of alkoxides of the alkaline-earth metals and magnesium increase in metallation reactions of ε-caprolactam in the order Mg < Ca < Sr < Ba.

Key words: ε-caprolactam, caprolactamates of magnesium, calcium, strontium, and barium, anionic polymerization of lactams.

One of the lines of progress of studies on anionic polymerization of lactams is the search for catalyst systems that make it possible to control the process rate and to modify the properties of polyamide formed, which may substantially extend the possibilities of the use of polyamide as a construction material. Caprolactamates of alkali and alkaline-earth metals are of great interest for anionic polymerization of lactams. The ionic character of alkaline-earth caprolactamates as well as of caprolactamates of Sr and Ba causes a high concentration of lactam anions, which are involved in the reaction of proton exchange with the polyamide chain when caprolactamates of these metals are used as catalysts of anionic polymerization of caprolactams. Caprolactamates of Mg and Ca are involved in anionic polymerization of lactams in the form of ionic pairs.[1,2]

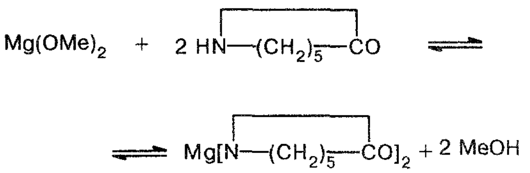
The use of caprolactamates of alkali metals and magnesium as well as halomagnesium lactams in the reaction injection molding (the RIM process) of products from homopolymers and block copolymers is known.[3–5] Note that it is possible to achieve maximum rates of anionic polymerization of lactams as well as to prepare polyamides with desired properties only when catalysts of high purity are used.[6]

Lactams of the general formula $\overline{HN-(CH_2)_n-CO}$, where n = 3, 5, and 11, are metallated in reactions of these lactams with metals,[7–10] metal hydrides,[3] alkoxides,[6,11,12] amides,[7,13] and organometallic[14–17] and complex compounds.[4,5,18–20]

In this work, we carried out systematic studies on synthesis of caprolactamates of alkaline-earth metals and magnesium using the known reactions as well as by developing new methods of synthesis. Comparative testing of the effect of caprolactamates obtained on their catalytic activity under conditions of anionic polymerization of lactams were performed.

Results and Discussion

With the aim of preparing caprolactamates of magnesium, calcium, strontium, and barium ($Mg(clm)_2$, $Ca(clm)_2$, $Sr(clm)_2$ and $Ba(clm)_2$) we systematically studied metallation of ε-caprolactam with alkoxide, alkyl, and hydride derivatives of the corresponding metals. Magnesium reacts most readily with methanol. The magnesium methoxide $Mg(OMe)_2$ formed is soluble in an excess of methanol, whereas the corresponding magnesium alkoxides obtained from other alcohols are insoluble. Magnesium methoxide forms mono- and tetrasolvates with an excess of methanol, which is the cause of its solubility in the alcohol. Completely desolvated magnesium methoxide is insoluble in hydrocarbon and alcohols. The exchange reaction of magnesium methoxide with ε-caprolactam (1) was studied in benzene and xylene at the boiling temperature with the evaporation of a mixture of methanol and xylene (benzene).



$$Mg(OMe)_2 + 2\,\overline{HN-(CH_2)_5-CO} \rightleftharpoons Mg[\overline{N-(CH_2)_5-CO}]_2 + 2\,MeOH \quad (1)$$

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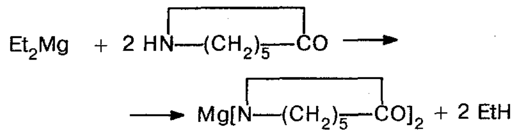
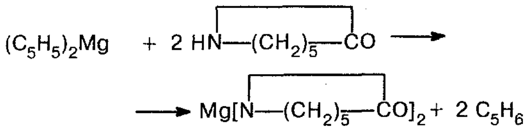
Both predesolvated magnesium methoxide and its mono- and tetrasolvates with methanol can be used in the reaction. The exchange reaction in benzene is not completed; methoxymagnesium caprolactamates of the varying composition with an inadequate catalytic activity under conditions of anionic polymerization of lactams are formed. In xylene, the exchange reaction is completed in 10—12 h at 140—142 °C.

Metallation of ε-caprolactam with organometallic compounds of magnesium, like Et_2Mg and $(C_5H_5)_2Mg$, is a good method for preparing Mg(*clm*)$_2$ (reactions (2) and (3)).



$$\mathrm{Et_2Mg + 2\,HN{-}(CH_2)_5{-}CO \longrightarrow Mg[N{-}(CH_2)_5{-}CO]_2 + 2\,EtH} \quad (2)$$



$$\mathrm{(C_5H_5)_2Mg + 2\,HN{-}(CH_2)_5{-}CO \longrightarrow Mg[N{-}(CH_2)_5{-}CO]_2 + 2\,C_5H_6} \quad (3)$$

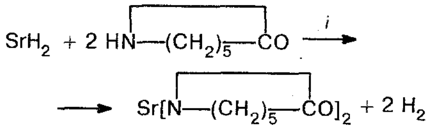
These reactions proceed readily and quantitatively in ether and hydrocarbon media and, hence, these reactions are good methods for obtaining pure Mg(*clm*)$_2$.

Calcium caprolactamate (Ca(*clm*)$_2$) was prepared by the reaction of $Ca(OEt)_2$ with ε-caprolactam in xylene upon boiling with distillation of an ethanol—xylene mixture. The reaction is completed in 8—10 h. The solubility of Ca(*clm*)$_2$ in hydrocarbon and ether solvents is limited, and the reaction product precipitates. A solution of calcium ethoxide in ethanol, its mono- or tetrasolvates with EtOH, as well as predesolvated calcium ethoxide may be used in the reaction.

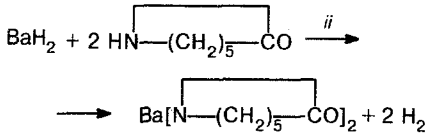
The exchange reactions of alkoxides of Sr and Ba with ε-caprolactam may be also successfully used to produce Sr(*clm*)$_2$ and Ba(*clm*)$_2$. When unsolvated $Ba(OMe)_2$ and $Sr(OMe)_2$ react with ε-caprolactam in xylene upon boiling, Ba(*clm*)$_2$ and Sr(*clm*)$_2$ are obtained in high yields.

Experimental data suggest that the reactivity of alkoxides of Group II metals in metallation of lactams increases in the order: Mg < Ca < Sr < Ba.

Magnesium hydride and calcium hydride are inactive to ε-caprolactam, whereas strontium and barium hydrides may be successfully used for the synthesis of their caprolactamates (reactions (4) and (5)).



$$\mathrm{SrH_2 + 2\,HN{-}(CH_2)_5{-}CO \xrightarrow{i} Sr[N{-}(CH_2)_5{-}CO]_2 + 2\,H_2} \quad (4)$$

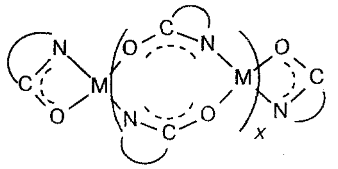


$$\mathrm{BaH_2 + 2\,HN{-}(CH_2)_5{-}CO \xrightarrow{ii} Ba[N{-}(CH_2)_5{-}CO]_2 + 2\,H_2} \quad (5)$$

i. 110—120 °C; xylene.
ii. 65 °C; THF.

Caprolactamates Sr(*clm*)$_2$ and Ba(*clm*)$_2$ are insoluble in hydrocarbon and ether solvents and, therefore, their purity substantially depends on the purity of initial hydrides.

The data on the structures and vibrational spectra of Mg(*clm*)$_2$, Ca(*clm*)$_2$, and Ba(*clm*)$_2$ were reported previously in our work.^{23} The differences in the IR and Raman spectra of solid caprolactamates of magnesium, calcium, and barium as well as in the IR spectra of their solutions are indicative of the differences in their structures. Ba(*clm*)$_2$ and Sr(*clm*)$_2$ have ionic structures, whereas Mg(*clm*)$_2$ and Ca(*clm*)$_2$ are partially covalent and have oligomeric chain structures with different types of N—CO groups (terminal and bridging groups).



M = Mg, Ca; *x* = *n* − 1

In solutions, Mg(*clm*)$_2$ and Ca(*clm*)$_2$ are associated through the formation of bridging N—CO groups. It was demonstrated that vibration frequencies of the bridging N—CO groups are in the region 1580—1620 cm^{-1}, and the frequencies of the terminal groups are in the region 1550—1580 cm^{-1}.

Table 1 gives comparative data on catalytic activities of caprolactamates of Group II metals, which we obtained. As evident from Table 1, all these compounds are active under conditions of anionic polymerization of ε-caprolactam. It should be noted that the catalytic activity of magnesium caprolactamate prepared from Et_2Mg and $(C_5H_5)_2Mg$ is higher than that of Mg(*clm*)$_2$ prepared from $Mg(OMe)_2$. Apparently, this is determined by the fact that when Mg(*clm*)$_2$ is synthesized from organometallic compounds of magnesium and ε-caprolactam, the reaction is not equilibrium, proceeds under mild conditions, and makes it possible to obtain the final product of a higher purity.

Experimental

All experiments including preparation of samples for IR and Raman spectroscopy were carried out under a dry argon atmosphere. All solvents used in experiments were purified and

Table 1. Catalytic activity of Mg, Ca, Sr, and Ba caprolactamates upon pseudoadiabatic polymerization of ε-caprolactam in the presence of toluylene diisocyanate as the activator[a]

Catalyst	Initial compounds[b]	t_p[c]	t_c[d]	t_f[e]
		min		
$Mg(clm)_2$	$Mg(OMe)_2$	25	45	62
	$MgEt_2$	14	22	35
	$Mg(C_5H_5)_2$ $C_5H_5TiCl_3$	11	15	34
$Ca(clm)_2$	$Ca(OEt)_2$	18	26	40
$Ba(clm)_2$	$Ba(OMe)_2$	23	27	33
$Sr(clm)_2$	$Sr(OMe)_2$	21	30	37

[a] Conditions of polymerization: 150 → 180 °C; the time during which the temperature was raised was 15 min; concentrations of the catalyst and the activator were 0.03 mol/L.

[b] In the synthesis of the catalyst from ε-caprolactam and the corresponding organometallic compound.

[c] t_p is the time of 50% conversion of ε-caprolactam to the polymer.

[d] t_c is the time of the onset of crystallization of the polymer.

[e] t_f is the time of the onset of shaping of the polymer block.

dried using conventional procedures. Alkoxides of Group II metals were prepared according to the known procedure.[21] Et_2Mg was prepared using symmetrization of EtMgBr with dioxane in an ether medium.[24] Dicyclopentadienylmagnesium $(C_5H_5)_2Mg$ was prepared using the reaction of metallic magnesium with cyclopentadiene in the presence of $C_5H_5TiCl_3$ as a catalyst.[25] Sr and Ba hydrides were prepared by hydrogenation of the corresponding metals in an autoclave at 320—380 °C at an H_2 pressure of 100—150 atm. The purities of the hydrides obtained were 92 % and 95 % for BaH_2 and SrH_2, respectively. ε-Caprolactam was twice recrystallized from anhydrous benzene, dried, and stored in a vacuum box at 40 °C (3 Torr), m.p. 68.5—69 °C. Mixtures of methanol and ethanol with xylene were analyzed by GLC on an LKhM-8MD instrument (a katharometer was used as the detector, He was used as carrier gas, a 2000 × 4 mm steel column, 5 % E-30 on Celite, 180 °C).

Synthesis of magnesium caprolactamate from $Mg(clm)_2$ and ε-caprolactam. $Mg(OMe)_2$ (6 g, 0.07 mol), ε-caprolactam (16.5 g, 0.146 mol), and anhydrous xylene (300 mL) were placed into a reactor flask. The reaction mixture was stirred upon boiling (142 °C) with slow distillation of a xylene—methanol mixture for 12 h. The reaction was monitored using GLC. When the reaction was completed (MeOH is absent in the distillate), the reaction mixture was filtered off, and the filtrate was evaporated to dryness *in vacuo* using a water jet pump at 80 °C. The white caramel-like product $Mg(clm)_2$ was obtained in 96 % yield (16.7 g). Found (%): C, 56.59; H, 7.91; N, 11.10; Mg, 9.77. $C_{12}H_{20}O_2N_2Mg$. Calculated (%): C, 57.99; H, 8.05; N, 11.28; Mg, 9.79. IR, ν/cm^{-1}: 1567, 1583 NCO (terminal) and 1601, 1611 NCO (bridging). In the Raman spectrum, the bands at 1554, 1560 and 1596, 1612 cm^{-1} correspond to these groups.

Synthesis of magnesium caprolactamate $Mg(clm)_2$ from Et_2Mg and ε-caprolactam. An ether solution of Et_2Mg (42.9 mL, 0.03 mol) with concentration of 0.7 mol/L was slowly added with stirring to a suspension of freshly distilled ε-caprolactam (6.8 g, 0.06 mol) in 70 mL of anhydrous ether at 20 °C; evolved ethane was collected in a gasometer after ether vapors were frozen out in a trap at −70 °C. When the addition of Et_2Mg was stopped, ethane was evolved in 97 % yield (1320 mL, 0.058 mol). After the reaction was completed, the solvent was evaporated *in vacuo* using a water jet pump, and the solid white residue was dried *in vacuo* (1 Torr) at 80 °C for 2 h to a constant weight. The white powdered product $Mg(clm)_2$ was obtained in 98 % yield (7.3 g). Found (%): C, 57.89; H, 8.34; N, 11.31; Mg, 9.37. $C_{12}H_{20}O_2N_2Mg$. Calculated (%): C, 57.99; H, 8.05; N, 11.28; Mg, 9.79. IR, ν/cm^{-1}: 1567, 1583 NCO (terminal) and 1601, 1611 NCO (bridging). In the Raman spectrum, bands at 1554, 1560 and 1596, 1612 cm^{-1} correspond to these groups.

Synthesis of magnesium caprolactamate $Mg(clm)_2$ from $(C_5H_5)_2Mg$ and ε-caprolactam in THF. A solution of $(C_5H_5)_2Mg$ in THF (92 mL, 0.0525 mol) with a concentration of 0.57 mol/L was slowly added with stirring to a suspension of freshly distilled ε-caprolactam (11.9 g, 0.105 mol) in 100 mL of anhydrous THF at 20 °C. When the addition of $(C_5H_5)_2Mg$ was stopped, the reaction mixture was allowed to stand at 20 °C for 0.5—1 h, and then the solvent was evaporated to dryness *in vacuo* using a water jet pump. The solid residue was dried *in vacuo* (1 Torr) at 100 °C for 3 h to a constant weight. The glassy dark-brown product $Mg(clm)_2$ was obtained in 98 % yield (12.8 g). Found (%): C, 57.68; H, 8.12; N, 11.25; Mg, 9.85. $C_{12}H_{20}O_2N_2Mg$. Calculated (%): C, 57.99; H, 8.05; N, 11.28; Mg, 9.79. Data on the IR and Raman spectra of the product obtained are similar to that previously described.

Synthesis of calcium caprolactamate $Ca(clm)_2$ from $Ca(OEt)_2$ and ε-caprolactam. $Ca(OEt)_2$ (10 g, 0.077 mmol), ε-caprolactam (17.4 g, 0.154 mol), and anhydrous xylene (350 mL) were placed into a reactor flask. The reaction mixture was stirred upon boiling, while a xylene—alcohol mixture was slowly distilled off for 10 h. The reaction was monitored using GLC. When the reaction was completed (EtOH is absent in the distillate), xylene was evaporated *in vacuo* (a water jet pump) to 1/3 volume and treated with a triple volume of cooled hexane. The residue was filtered off, washed with cold hexane, and dried *in vacuo* (1 Torr) at 100—120 °C for 2 h. The white powdered product $Ca(clm)_2$ was obtained in 91 % yield (18.52 g). Found (%): C, 53.81; H, 7.47; N, 10.46; Ca, 15.21. $C_{12}H_{20}O_2N_2Ca$. Calculated (%): C, 54.46; H, 7.56; N, 10.59; Ca, 15.16. The IR and Raman spectra of $Ca(clm)_2$ are analogous to those described previously for magnesium caprolactamate; absorption bands are in the region 1550—1650 cm^{-1}.[23]

Synthesis of calcium caprolactamate $Ca(clm)_2$ from metallic Ca, EtOH, and ε-caprolactam. Metallic Ca (10 g, 0.25 mol) was placed in a reactor flask, and a mixture of xylene (200 mL) and EtOH (60 mL) was added. The reaction mixture was boiled until Ca completely dissolved (~8 h). Then xylene (600 mL) was added to the reaction mixture, and excess alcohol was distilled off (GLC monitoring), then the temperature of the mixture was decreased to 50 °C, and freshly distilled ε-caprolactam (56.6 g, 0.5 mol) was added. The reaction of $Ca(OEt)_2$ with ε-caprolactam was carried out at 120—130 °C with stirring with a slow distillation of a xylene—alcohol mixture for 10 h. The reaction was monitored chromatographically. Further treatment was carried out as previously described. The white powdered product $Ca(clm)_2$ was obtained in 92 % yield (60.7 g). Found (%): C, 54.08; H, 7.50; N, 10.48; Ca, 15.10. $C_{12}H_{20}O_2N_2Ca$. Calculated (%): C, 54.46; H, 7.56; N, 10.59; Ca, 15.16.

Synthesis of barium caprolactamate $Ba(clm)_2$ from $Ba(OMe)_2$ and ε-caprolactam. A solution of ε-caprolactam (6.8 g, 0.06 mol) in 70 mL of anhydrous xylene was added with stirring to a suspension of $Ba(OMe)_2$ (6.0 g, 0.03 mol) in

100 mL of xylene. The reaction mixture was stirred upon boiling (142 °C) for 6 h with a slow distillation of a xylene—MeOH mixture. When the reaction was completed (MeOH is absent in the distillate), xylene was evaporated *in vacuo* (a water jet pump) to 1/3 volume and treated with a triple volume of cooled hexane. The precipitate formed was filtered off, washed with cooled hexane, and dried *in vacuo* (1 Torr) at 100—120 °C. The white powdered product Ba(*clm*)$_2$ was obtained in 90 % yield (9.75 g). Found (%): C, 38.82; H, 5.39; N, 7.55; Ba, 37.40. $C_{12}H_{20}O_2N_2Ba$. Calculated (%): C, 39.82; H, 5.39; N, 7.74; Ba, 37.97. IR, ν/cm^{-1}: 1560, 1574 (N—CO). The Raman spectrum contains one broad line at 1566 cm^{-1} in the region of N—CO.

Synthesis of barium caprolactamate Ba(*clm*)$_2$ from BaH_2 and ε-caprolactam. BaH_2 (2.7 g, 0.019 mol), ε-caprolactam (4.5 g, 0.04 mol), and anhydrous THF (100 mL) were placed into a reactor flask. The reaction mixture was stirred upon boiling until gas evolution was completed (6 h). When the reaction was completed, the reaction mixture was filtered off from unreacted BaH_2, and the filtrate was evaporated to dryness *in vacuo* using a water jet pump. The white caramel-like product was obtained in a yield of 7.2 g. When the product was dried *in vacuo* (1 Torr) at 100—120 °C, unreacted ε-caprolactam sublimated (1.1 g). The white caramel-like product Ba(*clm*)$_2$ was obtained in 89.5 % yield (6.1 g). Found (%): C, 38.45; H, 5.25; N, 7.44; Ba, 37.48. $C_{12}H_{20}O_2N_2Ba$. Calculated (%): C, 39.82; H, 5.53; N, 7.74; Ba, 37.97. The IR and Raman spectra were analogous to those described previously.

Synthesis of strontium caprolactamate Sr(*clm*)$_2$ from Sr(OMe)$_2$ and ε-caprolactam. A solution of ε-caprolactam (9.1 g, 0.08 mol) in 80 mL of xylene was added with stirring to a suspension of Sr(OMe)$_2$ (6.0 g, 0.04 mol) in 100 mL of anhydrous xylene. The reaction mixture was stirred upon boiling (142 °C) with a slow distillation of a xylene—MeOH mixture for 6 h. Further treatment was carried out using the same procedure as in the synthesis of barium caprolactamate from barium methoxide. The white powdered product Sr(*clm*)$_2$ was obtained in 95 % yield (11.85 g). Found (%): C, 45.08; H, 6.25; N, 8.75; Sr, 27.42. $C_{12}H_{20}O_2N_2Sr$. Calculated (%): C, 46.21; H, 6.41; N, 8.98; Sr, 28.11. IR, ν/cm^{-1}: 1560, 1574 (NCO). The Raman spectrum contains one broad line at 1566 cm^{-1} in the NCO region.

Synthesis of strontium caprolactamate Sr(*clm*)$_2$ from SrH_2 and ε-caprolactam. SrH_2 (1.4 g, 0.0156 mol), ε-caprolactam (3.6 g, 0.032 mol), and anhydrous xylene (50 mL) were placed into a reactor flask. The reaction mixture was stirred upon boiling until gas evolution was completed. After the reaction was completed, the mixture was filtered off from unreacted SrH_2, and the filtrate was evaporated *in vacuo* (a water jet pump) to 1/3 volume and treated with triple volume of cooled hexane. The precipitate formed was filtered off, washed with cooled hexane, and dried *in vacuo* (1 Torr) at 100—120 °C. Unreacted ε-caprolactam (0.3 g) sublimated. The white powdered product Sr(*clm*)$_2$ was obtained in 89.5 % yield (4.36 g). Found (%): C, 45.80; H, 6.35; N, 8.66; Sr, 27.85. $C_{12}H_{20}O_2N_2Sr$. Calculated (%): C, 46.21; H, 6.41; N, 8.98; Sr, 28.11. The IR and Raman spectra were described above.

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References

1. V. A. Kotel'nikov, L. B. Danilevskaya, V. V. Kurashev, M. N. Il'ina, V. S. Papkov, V. V. Gavrilenko, and L. A. Chekulaeva, *Vysokomol. Soedin., Ser. A*, 1993, **35**, 1257 [*Polym. Sci.*, 1993, **35** (Engl. Transl.)].
2. V. A. Kotel'nikov, L. B. Danilevskaya, V. V. Kurashev, I. O. Konova, V. V. Gavrilenko, and L. A. Chekulaeva, *Vysokomol. Soedin., Ser. A*, 1993, **35**, 1251 [*Polym. Sci.*, 1993 (Engl. Transl.)].
3. EP Pat. 147812, CO8G 18/66 (1984), *Chem. Abstr.*, 1985, **103**, 196573.
4. C. Kasumasa and K. Kobayaschi, JP Pat. 62263223, CO8G 69/18, *Chem. Abstr.*, 1988, **108**, 151579.
5. V. Kubanek, Z. Sterbacek, and J. Kralicek, CSR Pat. 235120, C08G 69/46.
6. J. Sebenda, A. Stiborova, L. Lochman, and Z. Bukac, *Org. Prep. Proced. Int.*, 1980, **12**, 289.
7. W. E. Hanford and R. M. Joyce, *J. Polym. Sci.*, 1948, **3**, 167.
8. T. Yasumoto, *J. Polym. Sci.*, 1965, **A-3**, 3301.
9. Pol. Pat. 129834, C08G 69/20, *Chem. Abstr.*, 1987, **107**, 154913.
10. N. Yoda and A. Miyake, *J. Polym. Sci.*, 1960, **43**, 117.
11. P. Cefelin and J. Sebenda, *Collect. Czech. Chem. Commun.*, 1961, **26**, 3028.
12. EP Pat. 238143, C08G 69/20, *Chem. Abstr.*, 1988, **108**, 76073.
13. Switzerland Pat. 631188, C08G 69/20.
14. US Pat. 4438034, C07D 223/10.
15. D. B. Malpass and L. W. Fannin, *J. Organomet. Chem.*, 1985, **93**, 2538.
16. R. B. Hodek and J. A. Seiher, US Pat. 4508646, C07D 223.
17. L. I. Zakharkin, V. V. Gavrilenko, V. V. Kurashev, L. A. Chekulaeva, V. A. Kotel'nikov, L. B. Danilevskaya, A. V. Markov, Yu. P. Yur'ev, M. A. Boyarkin, O. Zh. Zhibarov, and A. M. Egorov, USSR Pat. 1641824, C07 F3/02, C07D 223/10, *Byull. Izobr.*, 1991, 14 (in Russian).
18. H. Tani and T. Konomi, *J. Polym. Sci.*, 1968, **A-1**, **6**, 2295.
19. T. Konomi and H. Tani, *J. Polym. Sci.*, 1969, **A-1**, **6**, 2269.
20. V. A. Kotel'nikov, V. V. Kurashev, and T. M. Frunze, *Vysokomol. Soedin., Ser. A*, 1987, **29**, 2642 [*Polym. Sci. USSR*, 1987, **29A** (Engl. Transl.)].
21. D. Bredly, *Usp. Khim.*, 1978, **47**, 638 [*Russ. Chem. Rev.*, 1978, **47** (Engl. Transl.)].
22. N. Ya. Turova and A. V. Novoselova, *Izv. Akad. Nauk SSSR, Ser. Neorg. Mater.*, 1967, **3**, 3517 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1967 (Engl. Transl.)].
23. I. A. Garbuzova, L. A. Chekulaeva, L. B. Danilevskaya, A. V. Markov, V. A. Kotel'nikov, B. V. Lokshin, V. V. Gavrilenko, V. V. Kurashev, I. I. Tverdokhlebova, and O. I. Sutkevich, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 1570 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **40**, 1421 (Engl. Transl.)].
24. S. T. Ioffe and A. N. Nesmeyanov, *Metody elemento-organicheskoi khimii (Mg, Be, Ca, Sr, Ba)* [*Methods of Organometallic Chemistry (Mg, Be, Ca, Sr, Ba)*], Nauka, Moscow, 1963 (in Russian).
25. T. Saito, *Chem. Commun.*, 1971, 1422.

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