Macromol. Symp. ***153****, 197–208 (2000)*

SYNTHESIS AND CHARACTERIZATION OF DI- AND TRIBLOCK COPOLYMERS OF ε-CAPROLACTONE AND 1,3-BUTADIENE

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SUMMARY: Block copolymers of butadiene (B) and ε-caprolactone (CL) of PB-PCL and PCL-PB-PCL structure have been synthesized using step-by-step polymerization of monomers under the action of mono- and dilithium catalysts on the first step and by intermediate conversion of "living" polybutadienyllithium chains into alkoxide ones by means of ethylene oxide on the second step. Polymerization of CL was shown to be accompanied by reactions of intra- and intermolecular chain transfer reaction onto the polymer and by deactivation of active propagating alkoxide anions into practically inactive carboxylic ones. CL initiation mechanism is discussed, in particular, influence of polymeric nature of alkoxide initiators on the rate and efficiency of initiation reaction, compared to low-molecular species.

INTRODUCTION

Synthesis of block-copolymers, in particular, those containing both non-polar and polar, including polyester, hydrocarbon blocks is one of the most promising trends for synthesis of new polymer materials. Recently, synthesis of block-copolymers based on styrene and butadiene (hydrocarbon blocks) and CL (polyester block) of PS-PB-PCL, PS-PCL, and PB-PCL type, as well as their further modification have been reported[1,2] (PS is polystyrene block).

The block-copolymer molecules of such structure are amphiphylic; therefore these products may be used as compatibilizer while producing mixtures of incompatible polymers. Polycaprolactone is perfectly compatible with many polar polymers[1], while hydrocarbon blocks are compatible with non-polar ones, respectively.

The way of block-copolymers synthesis suggested in[1] is based on interaction of "living" polystyrene- or polybutadienyllithium (PSLi or PBLi) with CL. To avoid side reactions of chain transfer onto the monomer, which result in the formation of

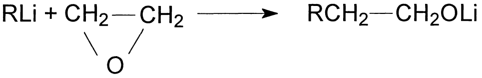
CCC 1022-1360/00/$ 17.50+.50/0

homopolymers, reactivity of "living" chains should be reduced. For this purpose, PSLi and PBLi should be preliminary treated with the excess of 1,1-diphenylethylene (DPE), thus transforming "living" chains into less active diphenylalkylenyllithium groups, which are not able to transfer the chain onto CL:

$$RLi + CH_2{=}C(Ph)_2 \longrightarrow RCH_2{-}C(Ph)_2Li \qquad (1)$$

For PSLi, addition of DPE occurs rather fast, while for PBLi it is slow. Therefore, before DPE is introduced, PBLi terminal groups are replaced for PSLi by inserting a little amount of styrene. However, addition of styrene to PBLi also occurs rather slowly, especially when there is some amount of unreacted butadiene.

It is well known [3,4] that CL can polymerize and copolymerize with other cyclic esters (lactides, carbonates) under alkoxide action, including lithium alkoxide, to yield high molar mass polymers. For PBLi and PSLi, "living" lithium active species can be fast and quantitatively converted into alkoxide form by ethylene oxide treatment.



$$RLi + \underset{\diagdown\,O\,\diagup}{CH_2{-}CH_2} \longrightarrow RCH_2{-}CH_2OLi \qquad (2)$$

It was interesting to find out whether this reaction could be useful for synthesis of di- and triblock-copolymers based on mono- and bifunctional precursors, respectively, i.e., mono- and dilithium polybutadiene. In addition, in this paper we are discussing the discrepancy in initiation of the CL polymerization with low-molecular initiators (1,1-n-hexyldiphenyllithium[1]) or cyclopentadienyl sodium[5]) and with polymeric precursors. This discrepancy has been found in[1]) and then confirmed in our experiments.

EXPERIMENTAL

Solvents (benzene and toluene) were treated according to technique[6]), then they were rectified using laboratory packed column of 1 m height to yield the solvent with admixtures content below 0.01% (GLC), and stored over CaH_2. Just before using, the solvent under argon flow was placed into the vessel containing CaH_2, degassed repeatedly, recondenced into the vessel containing a little amount of lithiumalkane, and was finally refrozen into the vessel for storing.

Butadiene was rectified on the column of 1 m height over triisobutylaluminum, with the fraction containing hydrocarbons C_3 being discarded. Then butadiene was degassed on the vacuum apparatus and distilled into the vessel containing lithiumalkane. After melting and appearance of characteristic light green color of living PB, butadiene was redistilled into the calibrated vessel.

ε-Caprolactone of Aldrich was stirred under argon over CaH_2 , then it was distilled and stored over CaH_2 under argon.

Sec-butyl lithium was synthesized by interaction of sec-butyl chloride with lithium in benzene in argon atmosphere.

2,5-dilithium hexane was synthesized according to technique$^{7)}$.

Butadiene was polymerized in benzene, in the one-liter reactor made of stainless steel and supplied with the mechanical stirrer, the jacket for thermal control, the drain valve, and loading union. The reactor is joined with high-vacuum apparatus via the valves, so that it can be evacuated of gas, filled with inert gas, loaded with reagents from measuring vessels. Initiator solutions were batched up into the reactor via the valve in the cap of the loading union using a syringe. Polymerization was performed at 30^0C. After completing butadiene polymerization, ethylene oxide was dosed to the reactor, and the reaction mixture was degassed after 10-15 minutes to eliminate excess of ethylene oxide.

To synthesize samples 1-5 (Table 1) solution of lithium polybutadienylethoxide was discharged under argon into the flask supplied with the union having a gasket of self-covering silicon rubber. Block copolymers were synthesized in the glass reactor equipped with stirrer, jacket, and unions for feeding argon and loading the reagents. Solution of lithium polybutadienylethoxide was fed to the reactor under argon with a syringe, heated to a desired temperature, and then CL was batched up with a syringe. After completing the reaction, the reactor was cooled, the solution neutralized by acetic acid, and the solvent was distilled in vacuum at 90-100^0C. Samples 6-9 were synthesized in the same metal reactor where lithium polybutadienylethoxide was produced, immediately after discarding the excess of ethylene oxide. CL was fed by a syringe via the valve, and solutions of block- copolymers were treated similar to the previous case.

Lithium tert-butylate (TBL) was synthesized by interaction of lithium with t-butanol excess under argon. After dissolving lithium, the alcohol excess was removed in vacuum at 100^0C. The resulting white powder was dissolved in toluene, and this solution was dosed by a syringe under argon into the glass reactor supplied with the stirrer. Then the necessary amount of toluene and CL was added into the reactor, and the reaction mixture was held at ambient temperature. After completion of the reaction, the mixture was neutralized by acetic acid, washed to neutrality, and the solvent was distilled in vacuum.

GPC analysis of polybutadiene precursors, block-copolymers and model CL oligomers was performed using Waters with refractometric detector. A set of two columns filled with Licrospher 500 and Silasorb 600 SPH was used, which provided linear calibration over polystyrene in the range of MM from 200 to $7{\cdot}10^5$. THF was used as an eluent; the rate of elution was 0.3 ml/min.

IR-spectra were recorded using Specord M-82. Composition of block copolymers was determined from the carbonyl group at 1773 cm^{-1} absorption band intensity (extinction coefficient in benzene is 630 l/mole·cm, PCL was used as reference).

Concentration of carboxylic groups in model CL oligomers was determined by conductometric titration of their isopropanol-acetone solution by isopropanol solution of KOH. Acetic acid was used as reference.

Mass-spectrum of CL dimer was measured in ethanol solution by means of ESI TOF Mass Spectrometry.

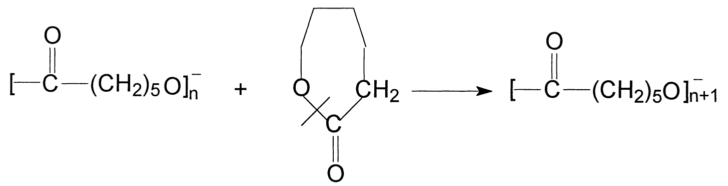
Results and Discussion

When block-copolymers are synthesized by step-by step polymerization of two or more monomers, maximum degree of molecular homogeneity of the resulting products is of a main importance. To provide this, the following requirements should be met:

- narrow MMD and about 100% functionality of the starting block;
- fast and quantitative initiation of the second and subsequent co-monomers polymerization without chain transfer onto the monomer during initiation;
- the absence or minimization of side reactions during polymerization of the second comonomer, i.e., “living” nature of polymerization.

For mono- and bifunctional polybutadienes the first requirement is easily met when secondary lithium alkanes (mainly, sec-butyl lithium), or di-secondary dilithium alkanes (e.g., 2,5-dilithium hexane) in hydrocarbon solvent are used as initiators[7,8)]. If CL is used as the second polar comonomer, nucleophilic properties of lithiumorganic active centers of hydrocarbon precursor should be reduced in order to eliminate the chain transfer onto the monomer due to the reaction of proton transfer onto the carbanion.

When alkali metals alkoxides or organometallic compounds initiate polymerization of lactones, the chain propagation occurs on the alkoxide anion as an active center with the splitting of monomer acyl-oxygen bond:



(3)

We assumed that the alkoxide terminal group, which forms fast and quantitatively upon PBLi and ethylene oxide interaction, is efficient enough in initiation of the CL polymerization without the chain transfer onto the monomer. Experiments are justified our expectations. The major molar mass characteristics of precursors and block-copolymers obtained are presented in Table1.

Table 1. Conditions of synthesis of PB-PCL (1-8) and PCL-PB-PCL (9) block-copolymers, their composition and molar mass characteristics.

#	T, °C / t, h	$\overline{M}_n$ / $\overline{M}_w / \overline{M}_n$ of initial PB	PB/PCL weight fraction ratio		$\overline{M}_w / \overline{M}_n$ of block-copolymer without oligomer fraction	Oligomer weight fraction in block-copolymer, %
			Calc.	Exp.		
1	70 / 2	3000 / 1.03	44 / 56	—	1.69	8.6
2	40 / 7	3000 / 1.03	40 / 60	37 / 63	1.61	9.6
3	50 / 1	3000 / 1.03	67 / 33	63 / 37	1.42	6.4
4	50 / 1	3000 / 1.03	80 / 20	78 / 22	1.29	< 1
5	30 / 0.5	3000 / 1.03	65 / 35	61 / 39	1.39	8.1
6	25 / 1	9000 / 1.1	60 / 40	65 / 35	1.33	8.6
7	25 / 0.25	5000 / 1.17	50 / 50	45 / 55	1.45	13.4
8	25 / 0.25	3000 / 1.03	30 / 70	40 / 60	1.90	21.6
9	25 / 0.33	5000 / 1.17	60 / 40	60 / 40	1.19	13.6

All samples lack a fraction soluble in heptane, i.e., butadiene homopolymer. This confirms a 100% efficiency of initiation CL polymerization by polymeric lithium alkoxide. But in fact, all samples contain a low-molecular fraction, which most probably consists of cyclic CL oligomers. They form due to intramolecular chain transfer reaction onto the own chain accompanied by detachment of the cyclic chain fragments[9-16)]. The last column of Table 1 shows the content of this fraction in the products.

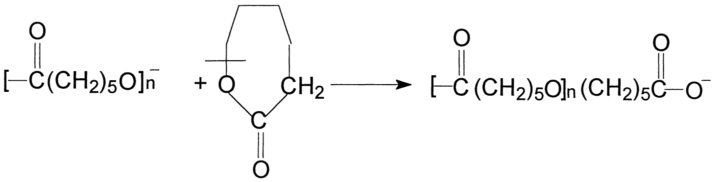
Some conclusions on the specific features of CL polymerization under the action of polymeric alkoxide initiator can be made from analysis of the Table 1 data. It is evident that oligomeric fraction hardly depends on temperature and duration of the reaction mixture exposure after addition of CL, but it tends to increase upon the increase of the monomer concentration. The resulting block copolymers usually have a broader MMD than that of the initial PB block. This broadening is the result of exchange reactions, which occur according to the mechanism of transfer the propagating active chain onto another (4) or onto itself $(5)^{15)}$. The latter results in the formation of cyclic products:

$$PBC_i^- + PBC_j \rightleftharpoons PBC_{i+k}^- + PBC_{j-k} \qquad (4)$$

$$PBC_i^- \rightleftharpoons PBC_{i-k}^- + C_k \qquad (5)$$

If there is no chain termination, these reactions should lead to redistribution of polyester blocks over lengths in block-copolymers. This results in finally the most probable MMD of polyester blocks. If no equilibrium is achieved in the system because of irreversible deactivation of active species (see below), the larger the blocks' length the broader is their MMD. Just this we observe in reality (compare, for example, MMD of polyester blocks of samples 8 and 9).

Formerly we show that CL is polymerized very slowly under sodium acetate action even at $200^0C^{16)}$. Taking into account this fact we assume that a “wrong” addition of the monomer to the propagating active center accompanied by splitting of the monomer cycle along alkyl-oxygen bond and by formation of inactive carboxylic anion is the most probable mechanism of irreversible deactivation.



(6)

In this case, the polymer should contain terminal carboxylate groups after neutralizing. To check this assumption, we have synthesized oligomeric CL with calculated MM values in the range from 1000 to 5000, using TBL as an initiator. The reaction occurred in toluene where concentrated TBL solutions (up to 0.3 mole/l) can be obtained. Content of carboxyl groups in oligomers was estimated after neutralizing using conductometric titration method. It was shown that all samples contain up to 90% of calculated amount of carboxyl groups (Table 2).

Table 2. Characteristics of the model CL-oligomers obtained under the action of TBL in toluene at 20°C.

Sample №	Concentration/ mol/l		Duration of reaction	M_p	$\overline{M}_n$		$\overline{M}_w/\overline{M}_n$ [a]	Content of COOH-groups/ equv/g$\cdot 10^3$	
	TBL	CL			Calc.	Exp.[a]		Calc.	Exp.
1	0.083	0.77	5 min	7250	1130	820	8.3[b]	0.88	0.19
2	0.047	1.29	10 min	9500	3200	830	8.0[b]	0.31	0.35
3	0.080	0.75	10 min	6500	1140	1500	3.95	0.88	0.62
4	0.280	2.36	24 h	1680	1030	333	4.9	0.97	0.98
5	0.030	1.24	1.5 h	27800	4800	4540	7.5	0.21	0.19
6	0.030	0.75	20 h	20450	2900	575	20.4[b]	0.34	0.33

[a] The polybutadiene calibration curve was used.

[b] The sample has bimodal MMD with a big oligomer fraction.

It is significant to note that the samples containing big fraction of oligomers have much lower values of $\overline{M}_n$ than the calculated ones. This is the result of the intramolecular chain transfer reaction proceeding in the reaction system.

However, the other way of formation of the end carboxylic groups in oligomers cannot be excluded a priory. This way assumes initiation of lactone polymerization by metal alkoxides via the proton separation from the monomer [5]. In this case terminal groups of macromolecules should not contain alkyl group from initiator. It can be easily checked by IR-spectrometry using TBL as an initiator containing methyl groups which absorption bands differ from those of polymer chain links and possess high enough coefficient of extinction. Fig. 1 shows IR-spectra of polylactone prepared by hydrolytic polymerization without the initiator and of oligomers with MM ~ 1000 prepared under the action of TBL as an initiator.

In the latter, there are absorption bands at 1366 and 1396 cm^{-1}, which can not be seen in the reference spectrum and which are referred to deformation vibrations of the methyl groups in tert-butyl unit[17].

Thus, the CL polymerization initiation mechanism under the action of lithium alkoxide is the same as chain propagation and consists in lactone ring opening via splitting acyl-oxygen bond.

While studying the model low molar mass PCL, we paid attention to their abnormal MMD. If the reaction system is neutralized in a few minutes after the monomer

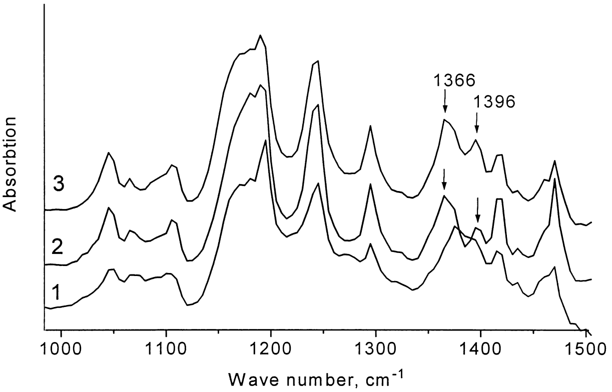


Fig.1: IR-spectra of the model PCL samples prepared by hydrolytic polymerization (1) and prepared under the action of TBL as an initiator (2 and 3). The legends of samples 2 and 3 are presented in Table2.

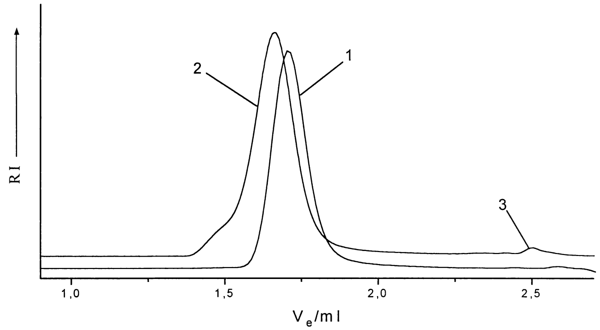


Fig.2: SEC curves of PB-precursor (1) and Sample 4 (2 and 3 peaks). 3 is oligomeric part. Column 250x4mm, Silasorb 600, THF eluent, 0.3 ml/min, 25°C. Refractometric detector. Sample 4 description see in Table 1.

introduction into the initiator solution, SEC curves have very characteristic view. They have a sharp peak, with MM values in maximum (M_p) being a few times higher than calculated ones, and a flattened slope into a low molar mass region. $\overline{M_n}$ values are close to calculated ones (Fig.2). If the reaction mixture is allowed to stand for a long time, MMD of the samples is rather broad, and in SEC curves there is rather distinct separation into oligomer homologs peaks in a low molar mass region (Fig.3).

This experimental observations can be explained if we assume that only a small part of initiator participates in fast initiation, and then initiation rate decreases drastically.

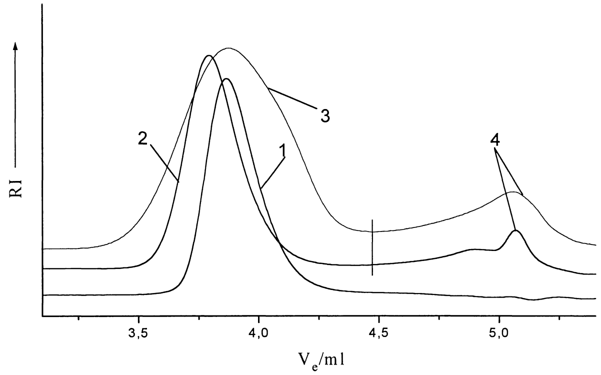


Fig.3: SEC curves of PB-precursor (1) for Sample 9 (2 and 4 peaks), Sample 8 (3 and 4 peaks). 4 is oligomeric part. 2 Columns 250x4mm, Lichrospher 500 and Silasorb 600; eluent THF, 0.3 ml/min, 25°C. Refractometric detector. Sample description see in Table 1.

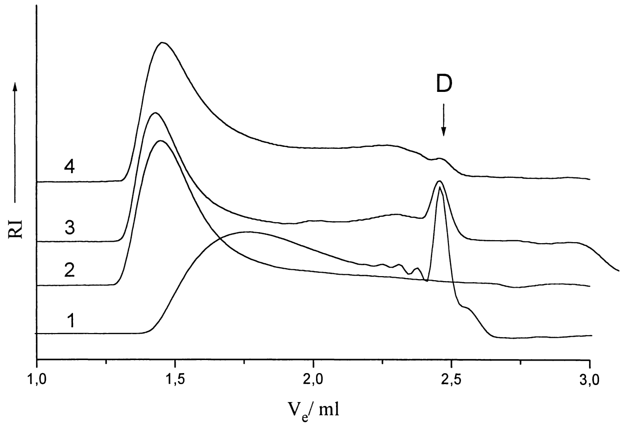


Fig. 4: SEC curves of the model PCL-samples. The numbers are in correspondence with the numbers in Table 2. The arrow denotes the cyclic dimer peaks. Column 250x4mm, Silasorb 600, THF eluent, 0.3 ml/min, 25°C. Refractometric detector. Sample description see in Table 2.

The further shift of MMD maximum and broadening of chromatograms can be evidently due to reactions of intra- and intermolecular chain exchange reactions, which competitiveness with chain propagation reaction increase in a great extent after the monomer consumption.

Yet, nothing similar occurs upon block-copolymer synthesis when polymeric initiator initiates CL polymerization. There are no low molar mass “tails” in the block- copolymer region, while oligomeric part appears immediately and does not change essentially upon long exposure and heating (see Table 1 and gel-chromatograms in Fig.4). Similar results have been obtained for block-copolymers of PS-PCL, PB-PCL and PS-PB-PCL type in1). So, different behavior of low molar mass and high-molecular initiators of the same structure of the active species seems to be regular.

We assume that different association degree of active species depending on the length of the chains they are attached to is responsible for this discrepancy. It is known that low-molecular alkali metal alkoxides are insoluble in hydrocarbons and in the most of aprotic organic solvents due to a strong dipole-dipole interaction.

Whatever is a mechanism of initiation, the original active species formed after addition of the CL molecule to the initiator is a primary lithium alkoxide. Such species evidently form polyassociates that are low active in the reaction of further monomer addition. If a rate of associate formation is commensurable with a rate of initiation and propagation, some part of active species is able to form rather long chains, while the major part of initiator is remained in associated low active form. Association degree of the polymer with highly polar terminal groups drops fast with the chain polymerization degree. For example, for polybutadiene having terminal zwitter-ionic ammonium sulfate groups, association degree of the chains drops from 40 to ~ 6 when MM of the polymer increases from 7600 to 77500(18). Reduction of association degree upon increase of the polymerization degree can be well described by calculations of conformation entropy of the star-like molecules taking into account the excluded volume (19). Thus, rather long macromolecules appear to be less associated and hence more active in reactions of both initiation and chain propagation. This mechanism can provide MMD of polymers shown in Fig.2.

For polymeric initiator, there is no chance for formation of low active associates with very high association degree, so all formed active species are of a similar reactivity, and all chains grow rather uniformly. The assumption that activity of polyassociates in intramolecular chain transfer reactions as well as initiation and propagation should be much lower than for the active species of low association degree seems to be quite reasonable. If it is true, it is become clear why there are no cyclic oligomers at the first stage upon initiation by low molar mass initiators (TBL), as well as accumulation of oligomer fraction together with block-copolymer formation upon initiation of CL polymerization with high-molecular initiators.

In all gel-chromatograms of oligomeric CL, one of the peaks (denoted as "D" in Fig. 4) is abnormally intensive in the region of oligomer homologs separation. During vacuum desiccation of block-copolymers at 90-100^{0}C sublimation of a colorless crystalline substance occurs. In the gel-chromatogram, the position of the peak of this substance corresponds exactly to the position of peak "D". ESI TOF Mass Spectrometry method revealed that the product is the cyclic CL dimer with mass number 228. This means that the attack of active propagating center on the last but one of the own polymer link is the most probable in intramolecular interchain exchange reaction. There are no enough data available to find out whether this preference has kinetic or thermodynamic reason.

Conclusion

It was shown that synthesis of rather homogeneous over structure and MMD well-defined di- and triblock copolymers of butadiene and ε-caprolactone is feasible using deactivation of "living" polybutadienelithium by preliminary treatment by ethylene oxide. It is more favorable for this purpose than use of 1,1-diphenylethylene, because it is not so time consuming, and no removal of a deactivating agent is necessary.

The data presented in this work and available in literature show that synthesis of block- copolymers based on "living" hydrocarbon polymers and CL is rather complicated process. Under these conditions CL polymerization does not correspond to classical concept of "living" polymerization. Formation of block-copolymer is accompanied by such of side reactions as chain termination reaction on the monomer because of a "wrong" attack of the propagating alkoxide anion on the alkyl-oxygen bond of the monomer with formation a low active carboxylate anion, and as reactions of interchain exchange proceeding via mechanism of intra- and intermolecular chain transfer reaction on polymer.

Initiation of CL polymerization by TBL consists in lactone ring opening via splitting acyl-oxygen bond with formation of alkoxide active species without any proton transfer reactions.

Initiation of CL polymerization by polybutadienelithium seems to be rather complicated, and its modeling using low-molecular initiators appears inadequate to initiation by polymer initiators because of the strong dependence of association degree of active species and their reactivity on the degree of polymerization. This finding being not so evident a priory.

Acknowledgements

Authors are grateful to International Science and Technology Center (Project 96-358) for the financial support. Authors are also indebted to V.I.Kozlovsky for CL dimer structure identification by ESI TOF Mass Spectrometry and V.P. Lodygina for IR-spectroscopic measurements.

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