Russian Chemical Bulletin, International Edition, Vol. 56, No. 7, pp. 1359—1362, July, 2007

Effect of the monomer concentration on piperylene cationic polymerization in the presence of the $TiCl_4$—trichloroacetic acid catalytic system

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The effect of the monomer concentration on the kinetics of cationic polymerization of piperylene in the presence of the $TiCl_4$—trichloroacetic acid catalytic system and molecular weight of the produced polymer was studied. At high monomer concentrations, the high-molecular-weight peak related to the formation of the branched fraction appears in the molecular weight distribution curve of the produced polymer.

Key words: piperylene, cationic polymerization, kinetics, molecular parameters, branching.

Existing concepts on the kinetic regularities of cationic polymerization of 1,3-dienes are disputable and contradictory in many aspects.[1,2] When studying the cationic polymerization of piperylene (1,3-pentadiene) in the presence of $AlCl_3$ in isopentane, a first-order reaction with respect to the monomer for *trans*-piperylene and the reaction order equal to 0.5 for the *cis*-isomer were observed.[3] At the same time, for piperylene polymerization on $AlCl_3$ in *n*-pentane, the data[4] indicating second-order kinetics with respect to the monomer were obtained for both *trans*-piperylene and a mixture of *cis*- and *trans*-isomers (34 and 66 mol.%, respectively). As for the effect of the piperylene concentration on the molecular parameters of the produced polymer, it is only known[5,6] that some increase in the number average molecular weight of polypiperylene is observed with an increase in the initial monomer concentration.

In the present work, we studied the effect of the piperylene concentration on the kinetics of cationic polymerization in the presence of the $TiCl_4$—trichloroacetic acid catalytic system and on the molecular parameters of the produced polypiperylene.

Experimental

Use was made of piperylene (trade mark P-1, produced at the plant "Sterlitamakskii SK," SK is synthetic rubber) with the following composition (wt.%): *trans*-isomer, 63.2; *cis*-isomer, 30.8; cyclopentene, 3.1; 2-methylbut-2-ene, 1.0; cyclopentadiene, 0.7; saturated hydrocarbons, the rest. Before polymerization piperylene was washed with water, dried with molecular sieves NaX, and distilled over CaH_2 in an argon flow. Piperylene contained the following microadmixtures (wt.%): water, less than $1 \cdot 10^{-3}$; carbonyl (based on acetone), less than $1 \cdot 10^{-3}$; peroxide (based on active oxygen), less than $1 \cdot 10^{-3}$; nitrogen-containing (based on dimethylformamide), $5 \cdot 10^{-4}$. The solvent (hexane) was dried over Al_2O_3 and distilled over CaH_2 in an argon flow. Trichloroacetic acid and $TiCl_4$ (Fluka) were used without additional purification.

Polymerization was carried out in an atmosphere of purified argon in glass ampules pre-heated under high vacuum. The catalyst was deactivated with a mixture of propylene oxide and methanol. The polymer was isolated by the distillation of the solvent and unreacted monomer from the ampules under high-vacuum conditions at 40 °C.

Isothermal conditions of the polymerization process should carefully be maintained especially in the initial period because of the high initial rate of piperylene polymerization and a substantial temperature effect on the polymerization kinetics and molecular parameters of polypiperylene formed.[6] In the present study, temperature changes during the whole polymerization process did not exceed 1—2 °C. For this purpose, the general volume of the reaction mixture in the ampules was decreased to 0.5—1 mL and stirring was carried out with a high rate.

The content of the insoluble gel fraction (GF) in the polymer was determined by extraction in the Soxhlet apparatus in boiling toluene for 24 h. The soluble fraction of the polymer, *viz.*, sol fraction (SF), was separated from the GF on a centrifuge from a polymer solution in hexane. The molecular parameters of the SF of the polymer were measured on a Waters—Alliance GPCV-2000 liquid chromatograph equipped with two detectors (viscosimeter and refractometer) and three styrogel columns with the pore size 500 (HR-2), 10^4 (HR-4), and 10^6 Å (HR-6) using toluene as the eluent with an elution rate of 1 mL min^{-1} at the temperature 30 °C. The C_1 and C_2 coefficients in the equation relating the molecular weight (M) and elution volume (V_e)

$$\log M = C_1 - C_2 V_e$$

were determined using calibration by the polystyrene standards (Waters).

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1310—1313, July, 2007.

Results and Discussion

The plots of the piperylene conversion *vs.* polymerization duration at different initial monomer concentrations in hexane are presented in Fig. 1. The high initial polymerization rate decreases with an increase in the polymer yield, which is related,[7] most likely, to the interaction of some active sites of the catalyst with the unsaturated fragments of the polymer chain of polypiperylene. The dependence of the initial polymerization rate on the initial monomer concentration derived from the data given in Fig. 1 is shown in Fig. 2. The polymerization rate detected 30 s after the process onset increases to a monomer concentration of 7.5 mol L^{-1} and then somewhat decreases. A similar dependence of the polymerization rate on the monomer concentration was observed[8] for the cationic polymerization of *cis,cis*-cycloocta-1,3-diene in the presence of the $TiCl_4$—H_2O catalytic system in methylene chloride. Based on the data obtained in the concentration interval from 1.0 to 7.5 mol L^{-1} (see Fig. 2), we determined the reaction order in hexane equal to 0.7. A fractional reaction order is due, most likely, to the use of a mixture of piperylene isomers as the monomer.

The results of determination of the molecular parameters of the polymer produced at different initial monomer concentrations and polymerization durations are presented in Table 1. For the low initial piperylene concentration (1.0 and 2.0 mol L^{-1}), the number average molecular weights (M_n) of polypiperylene somewhat increase and the polydispersity of the polymer (M_w/M_n) increases insignificantly. For the initial monomer concentration

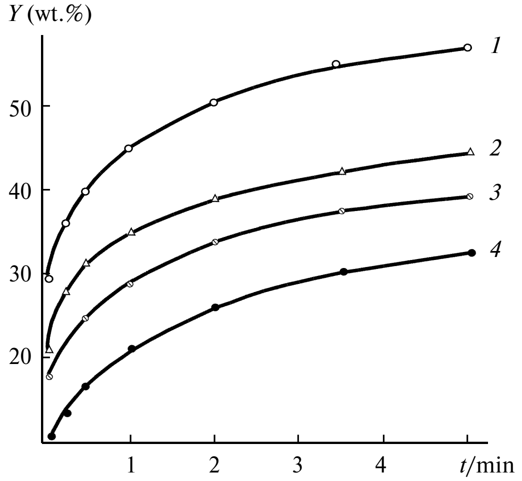

Fig. 1. Effect of the polymerization duration on the monomer conversion at the initial monomer concentration 1.0 (*1*), 2.0 (*2*), 4.0 (*3*), and 8.4 mol L^{-1} (*4*). Polymerization conditions: 20 °C, $[TiCl_4] = 0.02$ mol L^{-1}, $[C_2HCl_3O_2] = 0.04$ mol L^{-1}, hexane.

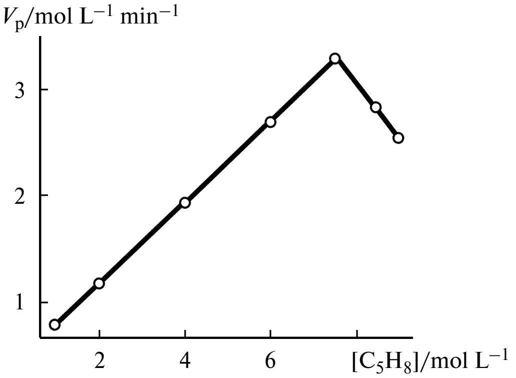

Fig. 2. Initial polymerization rate (V_p) *vs.* initial concentration of the C_5H_8 monomer.

Table 1. Dependences of the monomer conversion (Y) and molecular parameters of the SF on the polymerization duration (t) at different initial monomer concentrations (C_m)[a]

C_m /mol L^{-1}	t/min	Y (wt.%)	Molecular parameters of SF		
			$M_n \cdot 10^{-3}$	$M_w \cdot 10^{-3}$	M_w/M_n
1.0	0.25	35.8	1.8	3.5	1.9
	1.00	44.5	1.8	3.7	2.1
	2.00	49.5	1.7	3.7	2.2
	5.00	55.8	1.8	3.9	2.2
	30.00	67.6	1.9	4.3	2.3
2.0	0.08	20.8	2.1	4.2	2.0
	0.25	27.4	2.3	4.4	1.9
	1.00	34.2	2.5	5.2	2.1
	5.00	42.8	3.0	7.2	2.4
	30.00	58.5	3.2	8.5	2.7
4.0	0.08	17.5	2.1	3.6	2.1
	1.00	28.5	2.1	5.7	2.7
	5.00	37.1	2.9	8.8	3.0
	30.00	56.8	3.4	14.5	4.3
	180.00	79.2	3.5	27.6	7.9
	1440.00	90.3	4.2	54.8	13.0
6.0	0.08	15.6	2.8	5.9	2.1
	1.00	25.7	4.6	11.1	2.4
	5.00	37.1	4.8	14.8	3.1
	15.00	53.6	5.2	33.3	6.4
	180.00	75.7	5.4	130.1	24.1
	1440.00	88.5	5.2	199.2	38.3
7.5	0.50	21.8	3.0	7.4	2.5
	2.00	27.1	3.4	8.8	2.6
	15.00	51.2	5.1	30.6	6.0
	180.00	72.1	5.6	260.5	46.5
	1440.00	75.0[b]	5.2	212.7	40.9
	5760.00	78.7[c]	4.9	98.5	20.1
8.4	0.50	16.7	4.3	10.8	2.5
	2.00	25.0	4.8	12.3	2.6
	10.00	43.7	5.0	56.5	11.3
	30.00	57.3	6.1	137.4	22.5
	180.00	65.2	6.3	190.4	30.2
	1440.00	67.0[d]	4.5	118.5	26.3
	5760.00	68.0[e]	4.2	32.0	7.6

[a] For polymerization conditions, see Fig. 1. The content of the GF insoluble in the polymer is 2.3,[b] 12.7,[c] 18.2,[d] 28.9 wt.%,[e] and other samples contain no GF.

4.0 mol L^{-1}, when the monomer conversion increases, M_n of the polymer increases from $2.1 \cdot 10^3$ to $4.2 \cdot 10^3$ and the weight average molecular weight (M_w) increases from $3.6 \cdot 10^3$ to $54.8 \cdot 10^3$. The values of M_w and polydispersity increase rapidly starting at a monomer conversion of 79.2 wt.%. Similar dependences were found for higher initial concentrations of the monomer. For instance, the sharp increase in M_w and polydispersity for the monomer concentrations 6.0, 7.5, and 8.4 mol L^{-1} was detected at the monomer conversion 53.6, 51.2, and 43.7 wt.%, respectively.

For the monomer concentrations 7.5 and 8.4 mol L^{-1} and high monomer conversions (75.0, 78.7 and 67.0, 68.3 wt.%, respectively), the produced polypiperylene contains the insoluble GF along with the soluble SF (see Note to Table 1). Under these conditions, M_n, M_w, and polydispersity of the polymer in the soluble SF decrease from the moment of insoluble GF formation.

The chromatograms of polypiperylene produced at different conversions and the initial monomer concentrations 4.0 and 8.4 mol L^{-1} are presented in Figs 3 and 4. As can be seen from the data in Fig. 3, at the initial monomer concentration 4.0 mol L^{-1}, beginning from the monomer conversion 79.2 wt.%, the second maximum appears in the range of high molecular weights in the molecular weight distribution (MWD) curve (see Fig. 3, curve *3*). The height of the peak increases with the further increase in the monomer conversion (see Fig. 3, curve *4*). Thus, the sharp increase in the polydispersity of the produced polymer is associated with the appearance of the maximum in the MWD curve related to the high-molecular-weight fraction. For an initial monomer concentration of 8.4 mol L^{-1}, the peak of the high-molecular-weight fraction in the MWD curve appears already at the monomer conversion 43.7% (see Fig. 4, curve *2*). For the further increase in the monomer conversion, the content of the high-molecular-weight fraction in the polymer increases (see Fig. 4, curve *3*), whereas from the moment of appearance of the insoluble GF in the polymer the content of the high-molecular-weight fraction decreases sharply, which corresponds to a sharp decrease in the polydispersity of the polymer (see Fig. 4, curve *4*). A similar effect of the monomer conversion on the molecular heterogeneity of polypiperylene is observed[9] for cationic polymerization in toluene in the presence of the $TiCl_4—H_2O$ catalytic system.

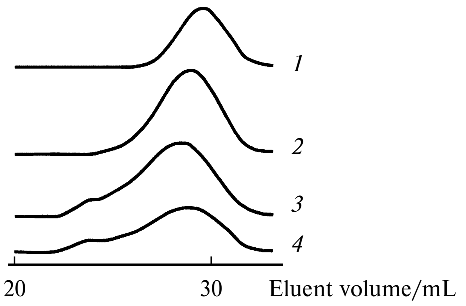

Fig. 3. Chromatograms of polypiperylene produced at the monomer conversion 17.5 (*1*), 37.1 (*2*), 79.2 (*3*), and 90.3 wt.% (*4*). The initial piperylene concentration is 4.0 mol L^{-1}.

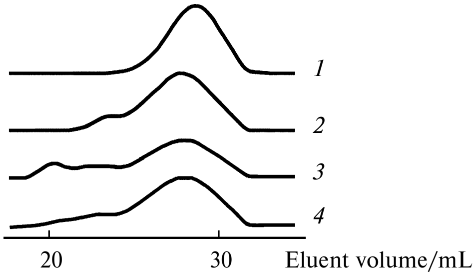

Fig. 4. Chromatograms of polypiperylene produced at the monomer conversion 16.7 (*1*), 43.7 (*2*), 65.2 (*3*), and 67.0 wt.% (*4*). The initial piperylene concentration is 8.4 mol L^{-1}.

Let us consider reasons for the appearance of the high-molecular-weight fraction in the polymer. This fraction represents, most likely, a branched polymer formed due to the reaction of chain transfer to the polymer. If the polymer concentration, at which the rapid increase in M_w and polydispersity occurs, is calculated using the data in Table 1, then this concentration related to a monomeric unit ranges from 3.2 to 3.8 mol L^{-1}. For the initial monomer concentrations 1.0 and 2.0 mol L^{-1}, this polymer concentration in the system is unattainable and, therefore, no jump in M_w and polydispersity is observed. In addition, using the data in Table 1, one can determine the ranges of the polymer concentration in the system (5.6—5.7 mol L^{-1}) when the insoluble GF begins to form in the polymer. These concentration ranges were attained only at the high initial monomer conversion (7.5 and 8.4 mol L^{-1}) and high monomer conversions.

To prove the presence of the branched fraction in the polymer, the logarithmic dependences of the intrinsic viscosity on the molecular weight of the polymer are shown in Fig. 5 for two polypiperylene samples produced at the initial monomer concentration 8.4 mol L^{-1} and piperylene conversion 25.0 and 57.3 wt.%. These dependences were obtained on a liquid chromatograph equipped with two detectors operating in parallel: refractometer and flow-type viscosimeter. As can be seen from the data in Fig. 5, *a*, for the polymer with the unimodal MWD the logarithmic change in the intrinsic viscosity is proportional to the molecular weight of the polymer in the whole interval of molecular weights. The calculation of the branching factor (*g* factor) performed using a known procedure[10] for this polymer gave $g = 1$. This indicates no branching. For polypiperylene produced at the monomer conversion 57.3 wt.%, the logarithmic dependence of the intrinsic viscosity on the molecular weight retains the linear character only in the region of the low-molecular-weight peak in the MWD curve (see Fig. 5, *b*). In the region of high

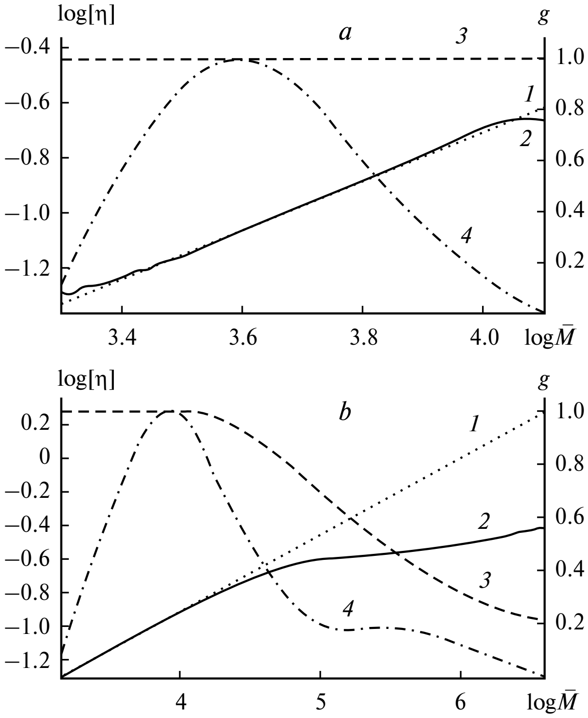

Fig. 5. Logarithmic plots of the intrinsic viscosity [η] (*1* is calculation; *2* is experiment) and branching factor *g* (*3*) *vs.* molecular weight ($\bar{M}$) and the MWD curve (*4*) of polypiperylene produced at C_m = 8.4 mol L^{-1} and monomer conversion 25.0 (*a*) and 57.3 wt.% (*b*).

molecular weights, a considerable deviation from linearity is observed and the *g* factor becomes lower than unity and decreases with an increase in the molecular weight. This indicates that the high-molecular-weight fraction is branched. It follows from the change in the character of the dependence of the branching factor on the molecular weight that the degree of branching increases with an increase in the molecular weight of the polymer.[10]

Thus, analysis of the dependences of the intrinsic viscosity on the molecular weight suggests that the appearance of the high-molecular-weight peak in the MWD curve of the SF of the polymer is related to the formation of branched macromolecules of the polymer. The degree of cross-linking of the polymer increases with the further increase in the monomer conversion, which finally results in the formation of the insoluble GF. Since mostly branched high-molecular-weight macromolecules react predominantly in cross-linking of polymer chains, these macromolecules are primarily extracted from the soluble SF of the polymer. This results in narrowing of the MWD and decreasing the average molecular weights of polypiperylene from the moment of gel formation onset (see Table 1).

The study of the effect of the monomer concentration on the kinetics of piperylene cationic polymerization in the presence of the $TiCl_4$—trichloroacetic acid catalytic system and on the molecular parameters of the produced polymer shows that at the monomer concentrations 1.0—4.0 mol L^{-1} the formed polypiperylene has the unimodal MWD and at the monomer concentrations 4.0—8.4 mol L^{-1} the MWD curve contains a high-molecular-weight peak associated with the formation of the branched fraction. The ranges of the polymer concentrations in the system, within which the branched and insoluble fractions are formed in polypiperylene, were determined.

References

1. J. P. Kennedy and E. Marechal, *Carbcationic Polymerization*, A Wiley—Intersci. Publ., New York, 1982, p. 510.
2. Yu. B. Monakov and G. A. Tolstikov, *Kataliticheskaya polimerizatsiya 1,3-dienov* [*Catalytic Polymerization of 1,3-Dienes*], Nauka, Moscow, 1990, 210 pp. (in Russian).
3. B. L. Irkhin, V. I. Ponomarenko, and K. S. Minsker, *Promyshlennost´ SK* [*Industry of Synthetic Rubber*], 1974, **9,** 18 (in Russian).
4. V. Bennevault-Celton, M. Delfour, and H. Cheradame, *Macromol. Chem. Phys.*, 2004, **205**, 1620.
5. J. M. Santarella, E. Rousset, S. Randriamahefa, A. Macedo, and H. Cheradame, *Eur. Polym. J.*, 2000, **36**, 2715.
6. S. A. Egoricheva, V. A. Rozentsvet, B. I. Pantukh, and R. M. Livshits, *Promyshlennost´ SK, shin i RTI* [*Industry of Synthetic Rubber, Tires, and General Mechanical Rubber Goods*], 1985, **11**, 7.
7. V. A. Rozentsvet, S. A. Egoricheva, Zh. A. Matveeva, B. I. Pantukh, and R. M. Livshits, *Promyshlennost´ SK, shin i RTI* [*Industry of Synthetic Rubber, Tires, and General Mechanical Rubber Goods*], 1987, **4**, 8 (in Russian).
8. M. A. S. Mondal and R. N. Уoung, *Eur. Polym. J.*, 1971, **7**, 523.
9. V. A. Rozentsvet and V. G. Kozlov, *J. Appl. Polym. Sci.: Appl. Polym. Symp.*, 1992, **51**, 183.
10. B. H. Zimm and R. W. Kilb, *J. Polym. Sci.*, 1959, **37**, 19.

Received November 2, 2006;
in revised form May 10, 2007