ISSN 1070-4272, Russian Journal of Applied Chemistry, 2008, Vol. 81, No. 10, pp. 1821–1830. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © A.L. Aleksandrov, E.R. Badamshina, G.A. Gorbushina, A.A. Grishchuk, A.S. Dzhalmukhanova, V.V. Komratova, I.S. Kochneva, A.I. Kuzaev, V.P. Lodygina, E.V. Stovbun, T.N. Fedotova, Ya.S. Estrin, 2008, published in Zhurnal Prikladnoi Khimii, 2008, Vol. 81, No. 10, pp. 1699–1709.

## MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

# "Dormant" Inhibitors of Urethane Type as Controllers of Temperature Modes of Styrene Polymerization

**A. L. Aleksandrov, E. R. Badamshina, G. A. Gorbushina, A. A. Grishchuk, A. S. Dzhalmukhanova, V. V. Komratova, I. S. Kochneva, A. I. Kuzaev, V. P. Lodygina, E. V. Stovbun, T. N. Fedotova, and Ya. S. Estrin**

*Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia*

Received February 28, 2008

**Abstract**—Urethanes based on a series of monoisocyanates and phenolic inhibitors of styrene radical polymerization, which release the initial phenolic inhibitor at elevated temperatures, were prepared and characterized. Some of these compounds meet the requirements to "dormant" inhibitors: they sharply decelerate thermally initiated high-temperature polymerization of styrene and do not noticeably affect the rate of low-temperature polymerization in the presence of an inhibiting substance. The possibility of preventing uncontrollable emergency situations by adding these compounds to the initial monomer was confirmed experimentally.

**DOI:** 10.1134/S1070427208100224

One of the most extensively used procedures for preparing polystyrene is polymerization in the bulk in large reactors, which is characterized by the complex behavior owing to the nonlinear dependence of the reaction rate on the temperature and reactant concentrations. The exothermic heat effect of polymerization has a positive feedback, i.e., both the reaction rate and heat release increase with temperature, which, in turn, causes further use in temperature. As a result, unstable states of the process and emergency situations arise, which are accompanied by an uncontrollable rise in the temperature of the reaction mass by tens of degrees and by a significant excess of the monomer conversion over the level permissible for the reactor.

In the commercial production of polymers, various mathematical models of the reactors are used, which allows development of automatic control systems providing the maximal productivity of the process. However, owing to the risk of uncontrollable emergency situations, the process is frequently performed under modes that are far from the optimum. Continuous polymerization of styrene is carried out in a cascade of reactors (with the volume of tens of cubic meters) to provide a gradual increase in temperature as the content of the monomer in the reaction mixture decreases [1]. The greatest danger of uncontrollable emergency situations is typical of the first reactor owing to the highest monomer concentration in the reaction mixture. Three main procedures are used to prevent the emergency with an uncontrollable temperature increase in the reactor: cooling of the reaction mixture by lowering the coolant temperature in the reactor jacket, addition of inhibitors that sharply decrease the polymerization rate, and emergency discharge of the reaction mixture into an external vessel with a solvent.

However, all the above procedures are noticeably inertial, i.e., they are characterized by slow elimination of the thermal and concentration gradients in the large reactor. Owing to the high inertia, prevention of the emergency situations in the case of local overheating may become impossible. The use of so-called "dormant" inhibitors (DIs) added to the reaction mixture before polymerization can be probably the optimal solution to this problem.

The effect of these inhibitors is as follows. A DI is inert at the polymerization temperatures. Upon an uncontrollable rise in the temperature above the permissible level, a DI exhibits the inhibition activity via its decomposition to components among which at least one component acts as a polymerization inhibitor or isomerization to give an active inhibitor. In this case, it is not necessary to supply the inhibitor to the over-heated area because DI is uniformly distributed in the reaction mixture from the very begining.

DIs were first suggested for controlling the photoinitiated polymerization of methyl methacrylate (MMA) in the form of large blocks [2]. As DIs were studied various compounds, such as nitroso compounds, hydrazine derivatives, saturated and unsaturated halogen derivatives, nitrites, and ammonium salts, which are activated and then inhibit polymerization even at 50–60°C. However, these compounds cannot be used in the case of styrene, because its polymerization is carried out at temperatures no less than 50°C at which all the above compounds act as polymerization inhibitors lowering the process rate and molecular weight of the polymer.

As is known, phenols and polyphenols (in particular, di- and triphenols) are efficient inhibitors of radical polymerization of styrene [3–5]. The inhibiting effect of these compounds is due to the fact that propagating polystyrene radicals detach a labile hydrogen atom from the hydroxy group of the inhibitor molecule and are thereby transformed into "dead" polymer molecules. The resulting oxyphenyl radicals do not interact with the monomer and thus cannot initiate the propagation of new polymer chains. If active hydrogen in the inhibitors can be blocked so that it will be activated only at relatively high temperatures, then its reactivity with respect to the polymer radicals at lower temperatures will be suppressed.

The most appropriate blocking procedure is conversion of phenols into urethanes in the reaction with isocyanates (DI of urethane type). The reaction of urethane formation can be represented as follows:

$$\mathrm{RNCO + HOR' \leftrightarrows RNHC(O)OR'}. \qquad (1)$$

At elevated temperatures, the reaction equilibrium is shifted to the left, and the temperature at which the equilibrium concentrations of isocyanate and phenol become noticeable depends on the structure of radicals R and R' [6].

Hydrogen atoms are more strongly bound with nitrogen atoms in the urethane group than with oxygen atoms in phenols. Hence, urethanes should not exhibit significant inhibiting activity at moderate temperatures [7].

Here, we describe the synthesis of some promising DIs of the urethane type and present characteristics of the resulting compounds and data on their effect on the kinetics of styrene polymerization under the isothermal conditions and on the thermal modes under the conditions of restricted heat exchange which model parameters of the heat exchange in large-volume reactors.

## EXPERIMENTAL

Styrene containing 99.9% main compound and stabilized with *p*-*tert*-butylpyrocatechol (0.001%) was washed to remove the inhibitor with a 10% NaOH solution (4 : 1 weight ratio). Then the monomer was washed with distilled water to neutral reaction. Washed styrene was dried over anhydrous $CaCl_2$. The dried monomer was distilled in a vacuum (44–45°C, 20 mm Hg) and stored in an argon atmosphere at –18°C. The monomer purity was determined by the kinetic method [8]. The reaction order of styrene polymerization with respect to initiator was found to be 0.5, which corresponds to the pure monomer.

Phenyl isocyanate (I-**I**), *m*-chlorophenyl isocyanate (I-**II**), *o*-chlorophenyl isocyanate (I-**III**), 2-ethylphenyl isocyanate (I-**IV**), 2,6-dimethylphenyl isocyanate (I-**V**), *o*-tolyl isocyanate (I-**VI**), and 6-chlorohexyl isocyanate (I-**VII**), all purchased from Aldrich, were distilled in a vacuum and stored in sealed glass ampules.

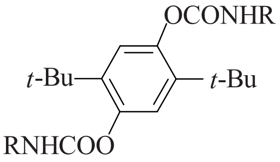
In this study, we used the following phenols: 2,5,7,8-tetramethyl-2-(4',8',12'-trimethyltridecyl)-6-chromanol (α-tocoferol) (P-**I**) purchased from Aldrich, was used without additional purification; 2,2,5,7,8-pentamethyl-6-chromanol, pure grade (P-**II**), mp 94–96°C, was recrystallized from petroleum ether; 1,2-dihydroxybenzene (pyrocatechol), pure grade (P-**III**), and 1,3-dihydroxybenzene (resorcinol), pure grade (P-**IV**), were sublimed in a vacuum at 100°C, mp 105–106 and 109–110°C, respectively; 1,4-dihydroxybenzene (hydroquinone), pure grade (P-**V**), was successively recrystallized from xylene, water, and acetonitrile, mp. 173.5–175.0°C, 1,4-dihydroxy-2,5-di-*tert*-butylbenzene (2,5-di-*tert*-butylhydroquinone), pure grade (P-**VI**), was precipitated with water from methanol and reprecipitated from ether with toluene, mp 217–219°C; and 4-*tert*-butyl-1,2-dihydroxybenzene (*p*-*tert*-butylpyrocatechol), pure grade (P-**VII**), was recrystallized from petroleum ether, mp 55–56°C.

Urethanes were prepared by the reaction of monoisocyanates with hydroxy compounds by reaction (1), using two standard procedures: (a) at [NCO]=[OH] at room temperature to complete consumption of

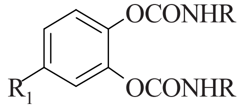
NCO groups and (b) at threefold excess of the isocyanate groups in the melt at 170°C, with subsequent distillation of excess isocyanate in a vacuum. In both procedures, the reaction was carried out in an inert gas atmosphere in the presence of $10^{-5}$ M urethane-forming catalyst (dibutyltin dilaurate, DBTDL). The resulting compounds were analyzed by IR spectroscopy for the reaction completeness judged from the absence of an intense absorption band at 2270 $cm^{-1}$, characteristic of the free isocyanate group. These compounds are crystalline compounds with mp from 20 to 271°C, except U-**IIIb** (Table 1). Urethanes were purified by recrystallization from toluene, the degree of purification was analyzed by reversed-phase chromatography.

The IR spectra were recorded on a Specord M-82 spectrophotometer: the spectra of compounds U-**Ia**–U-**Id**, U-**IIa**–U-**IIf**, and U-**IIIa**, in KBr pellets and those of compounds U-**IIIb** and U-**IIIc**, in capillary films prepared from solutions in chloroform.

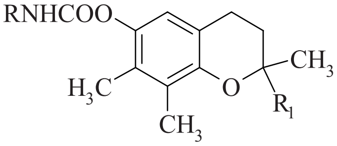
The structures of the resulting urethanes are as follows:



U-(**Ia–Id**):
R = 3-ClPh (a),
2-ClPh (b),
2-EtPh (c),
2,6-$(Me)_2$Ph (d)



U-(**IIa–IIf**):
R = Ph, $R_1$ = H (a);
R = Ph, $R_1$ = t-Bu (b);
R = 3-ClPh, $R_1$ = t-Bu (c);
R = 2-ClPh, $R_1$ = t-Bu (d);
R = 2-MePh, $R_1$ = t-Bu (e);
R = 6-$Cl(CH_2)_6$, $R_1$ = t-Bu (f)



U-(**IIIa–IIIc**):
R = 3-ClPh, $R_1$ = $CH_3$ (a);
R = 3-ClPh, $R_1$ = $[CH_2CH_2CH_2CH(CH_3)]_3CH_3$ (b);
R = 2,6-$(Me)_2$Ph, $R_1$ = $[CH_2CH_2CH_2CH(CH_3)]_3CH_3$ (c)

The characteristics of the urethanes prepared are listed in Table 1.

The chromatographic analysis of the initial compounds, urethanes, and diurethanes was carried out on a Milikhrom chromatograph equipped with a UV detector, using the reversed-phase procedure (2 × 80-mm column packed with Separon SGX C18, 6 μm, 5500 TP performance) with a water-methanol mixture as eluent. The optimal composition of the eluent providing determination of the maximal number of impurities at a sufficiently high resolution of the peaks was determined for each compound in the gradient mode, and analysis was carried out in the isocratic mode. Depending on the polarity of the compounds analyzed, the methanol : water ratio in the isocratic mode was varied from 30 : 70 to 90 : 10 at a flow rate of the eluent of 100 μl $min^{-1}$. The concentration of the compound analyzed in solution (in eluent or methanol) was up to 10 mg $ml^{-1}$ at a sample volume of 8 μl. The detection was performed in the single- or double-wave mode at 210 and 260 nm. For preliminarily identification of the impurities (if necessary), the spectra of each chromatographic peak in the 190–360 nm range were recorded in the stopped-flow mode.

The effect of potential DIs was preliminarily evaluated from the data on the kinetics of styrene polymerization at 50–70°C with azobis(isobutyronitrile) (AIBN) initiator and at 125 and 150°C without initiator (thermal initiation), in the presence of DI and without it. The measurements were carried out in isothermal calorimeters of the Tian–Calvet type. The reaction mixture in glass ampules was thoroughly degassed, sealed, and placed in calorimeter cells [9]. The signals of the calorimeters were recorded on a computer using an E-24 analog-digital converter (ADC); the signal from the E-24 ADC was recorded using a BEG program developed by Yu.A. Sokolov.

Nonisothermal thermal modes of the styrene polymerization under the conditions of restricted heat exchange in the absence and in the presence of DI were studied on a minireactor with restricted heat removal. The monomer containing either an initiator only or the initiator and DI was degassed and poured in a vacuum into a glass ampule 30 mm in diameter, equipped with a thermocouple well. The ampule was filled with argon, sealed off, and placed in the installation preliminarily heated to the temperature of an experiment. The thermal electromotive force of the copper–constantan thermocouple, whose cold ends were placed in a Dewar vessel containing an ice–water mixture, was recorded with E-24 ADC.

Nonisothermal thermal modes of the styrene polymerization were also simulated using 1- and 8-liter metallic reactors equipped with a stirrer and modified so as to provide the conditions of restricted heat exchange; the ratio of the heat-exchange area to the volume of the reaction mixture was about 1.5 $m^{-1}$, whereas

**Table 1.** Characteristics of urethanes

| Compound | Found, %<br>Calculated, % C | H | N | Cl | Name | Empirical formula | mp, °C | IR spectrum, ν, $\text{см}^{-1}$<br>UR = –OC(O)NH– |
|---|---|---|---|---|---|---|---|---|
| U-**Ia** | 62.70<br>63.52 | 5.21<br>5.71 | 7.25<br>5.29 | 14.8<br>13.39 | 2,5-Bis(*tert*-butyl)-1,4-dihydroxybenzene bis(3-chlorophenylcarbamate) | $C_{28}H_{30}Cl_2N_2O_4$ | 242–244 | 1732, 3304, 1540 (UR); 1595, 1507, 1405, 870, 811 (Ar); 2971, 2872, 1362 ($CH_3$) |
| U-**Ib** | 63.09<br>63.52 | 5.20<br>5.71 | 6.0<br>5.29 | 14.66<br>13.39 | 2,5-Bis(*tert*-butyl)-1,4-dihydroxybenzene bis(2-chlorophenylcarbamate), | $C_{28}H_{30}Cl_2N_2O_4$ | 212–214 | 1742, 1721, 3306, 1526 (UR); 3040, 1595, 1492, 1395 (Ar); 2966, 2917, 2873, 1440, 1375 ($CH_3$) |
| U-**Ic** | 72.87<br>74.39 | 7.50<br>7.80 | 6.60<br>5.42 | – | 2,5-Bis(*tert*-butyl)-1,4-dihydroxybenzene bis(2-ethylphenylcarbamate) | $C_{32}H_{40}N_2O_4$ | 201–203 | 1720, 1703, 3310, 1527 (UR); 3042, 1587, 1392 (Ar); 2960, 2902, 2873, 1416, 1361 ($CH_3$) |
| U-**Id** | 73.50<br>74.39 | 7.47<br>7.80 | 6.94<br>5.42 | – | 2,5-Bis(*tert*-butyl)-1,4-dihydroxybenzene bis (2,6-dimethylphenylcarbamate) | $C_{32}H_{40}N_2O_4$ | 270–273 | 1720, 3287, 1519 (UR); 3045, 3029, 1595, 1485, 1394 (Ar); 2963, 2928, 2873, 1437, 1377 ($CH_3$) |
| U-**IIa** | 68.36<br>68.96 | 5.04<br>4.63 | 9.65<br>8.04 | – | 1,2-Dihydroxybenzene bis(phenylcarbamate) | $C_{20}H_{16}N_2O_4$ | 193–196 | 1727, 3313, 1549, 1531 (UR); 1600, 1492, 695 (Ar); |
| U-**IIb** | 72.28<br>71.27 | 6.28<br>5.98 | 7.68<br>6.93 | – | 4-*tert*-Butyl-1,4-dihydroxybenzene bis-(phenylcarbamate), | $C_{24}H_{24}N_2O_4$ | 102–104 | 1731, 3332, 1542 (UR); 1601, 1499, 1406, 834 (Ar); 2968, 2871, 1363 ($CH_3$) |
| U-**IIc** | 61.03<br>60.90 | 4.97<br>4.68 | 6.21<br>5.92 | 15.70<br>14.98 | 4-*tert*-Butyl-1,4-dihydroxybenzene bis(3-chlorophenylcarbamate) | $C_{24}H_{22}Cl_2N_2O_4$ | 109–111 | 1719, 3334, 1541 (UR); 3048, 1611, 1505, 880 (Ar); 2961, 2937, 2863, 1460, 1361 ($CH_3$) |
| U-**IId** | 59.43<br>60.90 | 4.40<br>4.68 | 6.10<br>5.92 | 15.64<br>14.98 | 4-*tert*-Butyl-1,4-dihydroxybenzene bis(2-chlorophenylcarbamate) | $C_{24}H_{22}Cl_2N_2O_4$ | 218–221 | 1752, 3326, 1531 (UR); 3047, 1595, 1510, 1407 (Ar); 2966, 2870, 1440, 1360 ($CH_3$) |
| U-**IIe** | 66.47<br>72.20 | 6.02<br>6.53 | 6.80<br>6.48 | – | 4-*tert*-Butyl-1,4-dihydroxybenzene bis(2-methylphenylcarbamate) | $C_{26}H_{28}N_2O_4$ | 148–150 | 1745, 1726, 3310, 1537 (UR); 3028, 1591, 1506, 1410, 842, 812 (Ar); 2969, 2870, 1362 ($CH_3$) |
| U-**IIf** | 58.12<br>58.89 | 7.62<br>7.83 | 6.20<br>5.72 | 14.65<br>14.49 | 4-*tert*-Butyl-1,4-dihydroxybenzene bis(6-chlorohexylcarbamate) | $C_{24}H_{38}Cl_2N_2O_4$ | 65–66 | 1719, 3332, 1541 (UR); 1505, 1410, 880 (Ar); 731 (C–Cl); 2959, 2936, 2862, 1467, 1361 ($CH_3$) |
| U-**IIIa** | 67.43<br>66.75 | 6.21<br>6.16 | 4.40<br>3.89 | 9.84<br>9.85 | 2,2,7,8-Tetramethylchroman-6-ol 3-chlorophenylcarbamate | $C_{20}H_{22}ClNO_3$ | 158–160 | 1751, 3311, 1530 (UR); 1595, 1481, 1405, 787 (Ar); 2978, 2930, 2865, 1456, 1387 ($CH_3$) |
| U-**IIIb** | –<br>73.72 | –<br>9.19 | –<br>2.46 | –<br>6.22 | 2,7,8-Trimethyl-2-(4,8,12-trimethyltridecyl)chroman-6-ol 3-chlorophenylcarbamate | $C_{35}H_{52}ClNO_3$ | Waxy | 1708, 3273, 1541 (UR); 3012, 1598, 1505, 1415 (Ar); 2952, 2928, 2868, 1456, 1377 ($CH_2$, $CH_3$) |
| U-**IIIc** | –<br>78.81 | –<br>10.19 | –<br>2.48 | – | 2,7,8-Trimethyl-2-(4,8,12-trimethyltridecyl)chroman-6-ol 2,6-dimethylphenylcarbamate | $C_{37}H_{57}NO_3$ | 19–21 | 1693, 3233, 1523 (UR); 3021, 1600, 1505, 1415 (Ar); 2954, 2929, 2869, 1456, 1371 ($CH_2$, $CH_3$) |

for 15 $m^3$ industrial reactors this ratio is close to 2 $m^{-1}$. Experimentally, we selected the conditions at which the system passes into the high-temperature mode in the absence of DI. In the nonisothermal tests we also used AIBN initiator at a common concentration of 0.02 M.

In all the cases, unless otherwise indicated, the concentrations of the inhibitors and potential DIs were also 0.02 M.

The molecular-weight distribution (MWD) of polystyrenes was determined at 25°C on a Waters chromatograph with a refractometric detector [10] and a tetrahydrofuran eluent at 1.2 ml $min^{-1}$ flow rate. The volume of the sample was 2 ml, and the concentration of the compound being analyzed in solution was 0.3–0.4 wt %. We used three Styrogel columns (10 × 1000 mm) calibrated using polystyrene references with a porosity of $3 \times 10^3$, $3 \times 10^4$, and $3 \times 10^5$ Å.

A distinctive feature of styrene is that it is capable of thermally initiated polymerization at a rather high temperature (above 90–100°C) [11, 12]. This means that, if the control over the process (performed at moderate temperatures in the presence of initiating substance) is lost, further polymerization and, thus, uncontrollable temperature increase can occur even after complete consumption of the initiator. Just in these cases the use of DIs may become the only way to avoid uncontrollable emergency situations.

Apparently, DIs of the urethane type can be synthesized only from such proton-donor compounds that rather effectively decelerate radical polymerization. Therefor, we estimated the inhibiting power of a series of phenols.

It should be noted that polymerization of styrene is, as a rule, accompanied by the gel effect, which is manifested in a manyfold increase in the reaction rate in the course of the process passing from the bimolecular chain termination to the diffusion-controlled stage. Transition of the polymerization to the high-temperature uncontrollable mode is the most probable just in the step of the gel effect, when the polymerization rate is the highest, whereas the intensity of the heat exchange decreases owing to the rapid increase in the viscosity of the reaction mixture [13]. Therefore, the inhibiting power of the compounds in question was evaluated using two parameters: $\varphi_0 = W_0/W_{0x}$ and $\varphi_m = W_m/W_{mx}$, where $W_0$ and $W_{0x}$ are the reduced initial rates of polymerization and $W_m$ and $W_{mx}$ are the maximal reduced rates of polymerization (at similar conversions) in the absence and in the presence of the inhibitor, respectively. The parameters of the inhibiting power of phenols in styrene polymerization are listed in Table 2.

**Table 2.** Inhibition parameters $\varphi_0$ and $\varphi_m$ of phenols in styrene polymerization

| Potential inhibitor | $\varphi_0$ | | $\varphi_m$ | |
|---|---|---|---|---|
| | at indicated temperature, °C | | | |
| | 60 | 125 | 60 | 125 |
| P-**I** | 1.05 | 2.5 | a* | 20.6 |
| P-**II** | 2.03 | 1.5 | 61.2 | 15.2 |
| P-**III** | 2.08 | 1.40 | 26.32 | 3.0 |
| P-**IV** | 1.35 | 0.9 | 0.4 | 1.1 |
| P-**V** | 1.68 | 1.2 | 4.3 | 1.3 |
| P-**VI** | b** | 2.0 | b** | 10.0 |
| P-**VII** | b** | 1.5 | b** | 7.1 |

* Reaction is terminated at the conversion $\alpha = 0.3$.

** Strong inhibition, almost no polymerization is observed.

As can be seen, phenols P-**IV** and P-**V** do not noticeably inhibit polymerization of styrene at temperatures of 60°C and higher. Compounds P-**III**, P-**VI**, and P-**VII** more strongly inhibit the process in the case of initiated polymerization at 60°C, whereas at thermally initiated polymerization (125°C and higher) chromanols P-**I** and P-**II** are the most effective.

Based on the data on the inhibiting power of the above compounds (Table 2), we chose phenols P-**I**–P-**III**, P-**VI**, and P-**VII** for the synthesis of urethane-type DIs.

As shown above, the decomposition of urethane-type DIs with liberation of the active inhibitor should occur in a certain temperature range. We have shown previously [14] that neat urethanes based of phenols start to decompose to the initial components at a noticeable rate [reaction (1)] at temperatures higher than 200°C. Apparently, such compounds cannot be used as DIs. At the same time, as shown in [14], decomposition of these compounds with water [reactions (2)–(4)] or aliphatic alcohols [reaction (5)], especially in the presence of tin-containing organic catalysts (e.g., DBTDL), can occur at significantly lower temperatures with the release of the initial phenol. In these reactions, the isocyanates are converted into urea derivatives (reaction with water) or alkyl urethanes (reaction with alcohols), and reactions (2)–(5) are almost irreversible.

**Table 3.** Parameters of inhibition of styrene polymerization with urethanes at 60°C

| Compound | $\varphi_0$ | $\varphi_m$ | Compound | $\varphi_0$ | $\varphi_m$ |
|---|---|---|---|---|---|
| U-**Ia** | 1.11 | 1.43 | U-**IId** | 1.78 | 4.35 |
| U-**Ib** | 1.08 | 1.23 | U-**IIe** | 1.04 | 1.98 |
| U-**Ic** | 1.25 | 2.67 | U-**IIf** | 1.33 | 1.15 |
| U-**Id** | 1.39 | 2.80 | U-**IIIa** | 1.0 | 1.54 |
| U-**IIa** | 1.25 | 1.85 | U-**IIIb** | 1.1 | >100* |
| U-**IIb** | 1.11 | 2.56 | U-**IIIc** | 1.0 | >100* |
| U-**IIc** | 1.07 | 1.33 | | | |

* Polymerization is virtually terminated at 30–35% conversion.

$$\mathrm{RNHCOOAr + H_2O \rightarrow RNHCOOH + ArOH}, \qquad (2)$$

$$\mathrm{RNHCOOH \rightarrow CO_2 + RNH_2}, \qquad (3)$$

$$\mathrm{RNHCOOAr + RNH_2 \rightarrow RNHCONHR + ArOH}, \qquad (4)$$

$$\mathrm{RNHCOOAr + HOR' \rightarrow RNHCOOR' + ArOH}. \qquad (5)$$

Taking into account that the monomers for radical polymerization are not thoroughly dried to remove moisture, we assumed that the activation of DIs can occur, depending on their structure and operation conditions, in the acceptable temperature range.

The inhibiting activity of DIs was evaluated by two procedures. In the first procedure, we compared the isothermal kinetics of polymerization of the polymer (in particular, styrene) in the presence and absence of a compound in question. The ideal DI should not affect the process at moderate temperatures, but should decelerate polymerization at elevated temperatures.

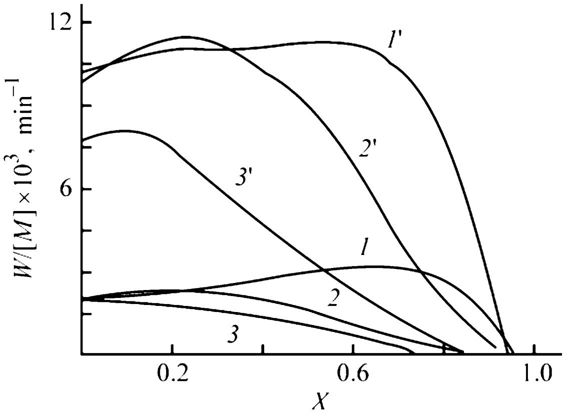


**Fig. 1.** Reduced rate of thermal polymerization of styrene $W/[M]$ vs. conversion $X$ (*1*, *1'*) in the absence of additives and in the presence of urethanes (*2*) U-**IIIc**, (*3*) U-**IIIb**, (*2'*) U-**IIIa**, and (*3'*) U-**IIIb**; concentration of urethanes $2\times10^{-2}$ M. Temperature, °C: (*1*–*3*) 125 and (*1'*–*3'*) 150.

The second procedure requires that similar comparative experiments should be performed in reactors with restricted heat exchange, in which nonisothermal modes of polymerization are provided and uncontrollable emergency situations are simulated. In this case, polymerization in the presence and absence of DIs should be performed in similar thermal modes of polymerization in a comparatively low-temperature range. In the high-temperature range, a certain decrease in temperature should be observed in styrene polymerization in the presence of DI as compared to the control experiment.

The inhibition parameters of styrene polymerization at 60°C for the urethanes prepared are listed in Table 3. As can be seen, at 60°C almost all the urethanes only slightly affect the initial and maximal rate of polymerization, except urethanes U-**IId**, U-**IIIb**, and U-**IIIc**. For example, urethane U-**IId** suppresses the gel effect and does not noticeably affect the initial polymerization rate, whereas urethanes U-**IIIb** and U-**IIIc** do not affect the initial rate and strongly inhibit polymerization at a conversion of about 30%. Nevertheless, the thermal polymerization of styrene in the presence of urethanes U-**IIIb** and U-**IIIc** was also studied.

The data on the effect of urethanes U-**IIIb** and U-**IIIc** on thermal polymerization, presented in Fig. 1, indicate that compound U-**IIIb** more effectively inhibits styrene polymerization at 125°C than does compound U-**IIIc**; it permanently decreases the polymerization rate and completely terminates the process at a 70% conversion. The inhibiting power ofprocess at urne U-**IIIb** is greater than that of U-**IIIa** at 150°C.

Our experimental data show that, at 125°C, urethanes U-**IIc** and U-**IId** do not noticeably affect the initial rate and noticeably decelerate the polymerization in the course of the process, whereas compound U-**IIa** only slightly affects the reaction rate throughout the process. Urethane U-**IIb** at elevated temperatures first significantly raises the initial rate, but after a 30% conversion is attained, it does not noticeably affect the polymerization rate. Hence, urethanes U-**IIa** and U-**IIb** are unsuitable as DIs. Compound U-**IIf** does not affect the initial rate of styrene polymerization, but it suppresses the gel effect, and the highest conversion attained in this case is 85%.

As noted above, the decomposition of urethanes with the release of the free inhibitor at temperatures

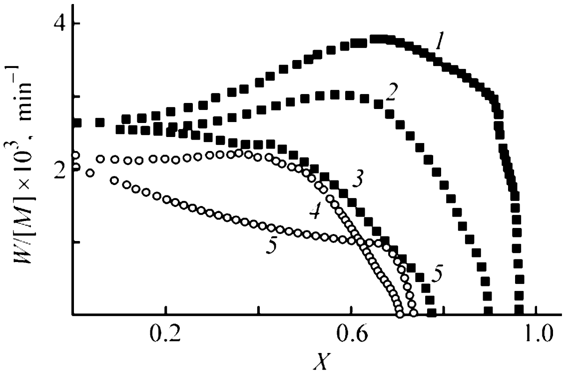


**Fig. 2.** Reduced rate of thermal polymerization of styrene $W/[M]$ vs. of conversion $X$ (*1*) in the absence of additives and in the presence of (*2*) urethane U-**Id**, (*3*) inhibiting formulation based on urethane U-**Id**, (*4*) urethane U-**IIc**, and (*5*) inhibiting formulation based on urethane U-**IIc**. $T = 125°C$, $[U] = [BuOH] = 2 \times 10^{-2}$ M, $[DBTDL] = 10^{-5}$ M.

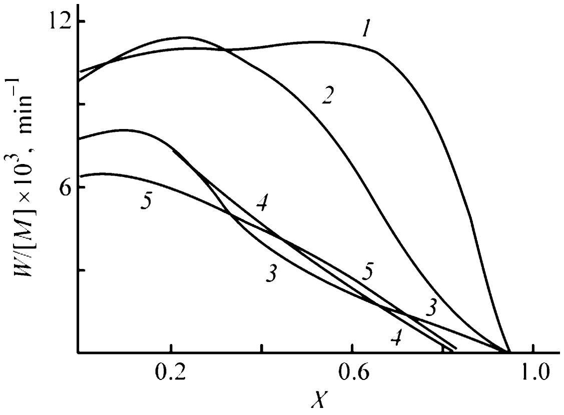


**Fig. 3.** Reduced rate of thermal polymerization of styrene $W/[M]$ vs. conversion $X$ (*1*) in the absence of additives and in the presence of (*2*) urethane U-**IIIa**, (*3*) inhibiting formulation based on urethane U-**IIIa**, (*4*) urethane U-**IIe**, and (*5*) inhibiting formulation based on urethane U-**IIe**. $T = 150°C$, $[U] = [BuOH] = 2 \times 10^{-2}$ M, $[DBTDL] = 10^{-5}$ M.

lower than 200°C proceeds at a significant rate only in the exchange reactions with proton-donor compounds and, in particular, with water and alcohols. This fact suggests that the inhibiting effect of urethanes on the styrene polymerization at 125–150°C is probably due to the exchange reactions with water present in the monomer.

The temperature at which inhibitors of the phenolic type are liberated from urethanes can be additionally lowered (i.e., the DI performance can be improved) by using the “inhibiting formulation” containing a urethane-type DI, a proton-donor compound, and a catalyst.

To confirm the above assumption, we studied the isothermal polymerization of styrene as influenced by the inhibiting compositions based on urethanes U-**Id**, U-**IIc**, U-**IIe**, and U-**IIIa**, containing *n*-butanol (BuOH) taken in equimolar amount to urethane (~0.02 M) and DBTDL (~$10^{-5}$ M). At 60°C, these inhibiting formulations do not noticeably affect the initial rate of polymerization, but slightly diminish its maximal rate (i.e., decrease the gel effect).

The data on the inhibiting effect of some of the above formulations at 125 and 150°C (Fig. 2, curves *2* and *3*, *4* and *5*; Fig. 3, curves *2* and *3*) show that, compared to urethanes, they are actually more effective DIs of the isothermal polymerization of styrene. At the same time, under the given experimental conditions, urethane U-**IIe** exhibits the highest activity in the absence of proton donor, which does not noticeably affect the performance of this urethane (Fig. 3, curves *4*, *5*). Our special tests showed that, under the isothermal conditions in the absence of urethanes, neither *n*-butanol nor DBTDL affect the rate of styrene polymerization in the entire temperature range studied (60–150°C).

Since the MWD parameters are the decisive factors affecting the polymer properties, we studied the effect of some inhibitors and urethane-type DIs on the molecular weight (MW) of the resulting polystyrene (Table 4). As can be seen, the additives inhibiting the styrene poly-

**Table 4.** MWD parameters of polystyrenes prepared in the presence of some inhibitors and DIs

| Additive | $M_n \times 10^{-3}$ | $M_w \times 10^{-3}$ | $M_w/M_n$ | $M_z \times 10^{-3}$ | $M_z/M_w$ |
|---|---|---|---|---|---|
| 60°C (initiated polymerization) | | | | | |
| – | 128 | 528 | 4.13 | 1027 | 1.95 |
| P-**V** | 110 | 290 | 2.64 | 540 | 1.84 |
| P-**III** | 145 | 313 | 2.15 | 530 | 1.70 |
| P-**VII** | 102 | 490 | 4.80 | 1093 | 2.23 |
| U-**IIa** | 195 | 422 | 2.15 | 713 | 1.69 |
| U-**IIc** | 177 | 550 | 3.11 | 1050 | 1.91 |
| U-**IId** | 177 | 560 | 3.16 | 1060 | 1.89 |
| 125°C (thermal polymerization) | | | | | |
| – | 145 | 390 | 2.69 | 640 | 1.64 |
| P-**I** | 64 | 161 | 2.52 | – | – |
| P-**VI** | 34 | 133 | 3.97 | 276 | 2.07 |
| P-**III** | 102 | 225 | 2.50 | 453 | 1.77 |
| P-**VII** | 66 | 177 | 2.68 | 332 | 1.88 |
| U-**IIa** | 150 | 361 | 2.40 | 608 | 1.68 |
| U-**IIc** | 133 | 313 | 2.49 | 594 | 1.79 |
| U-**IId** | 112 | 295 | 2.63 | 546 | 1.85 |
| U-**IIIb** | 95 | 253 | 2.67 | – | – |

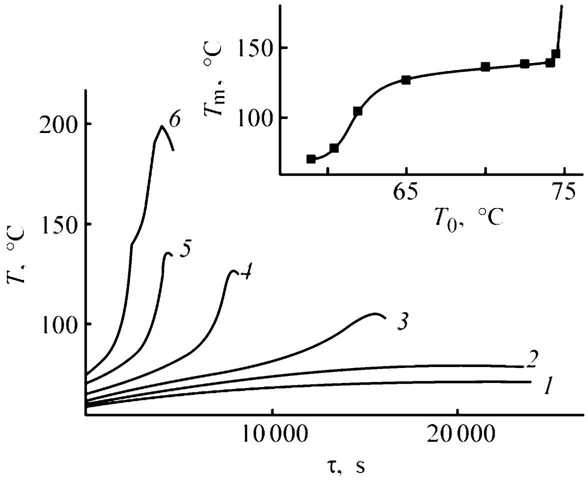


**Fig. 4.** Temperature curves of styrene polymerization in glass ampules in the mode of restricted heat exchange. ($T$) Temperature and ($\tau$) time; the same for Figs. 5 and 6. $T_0$, °C: (*1*) 59, (*2*) 60.5, (*3*) 62, (*4*) 65, (*5*) 70, and (*6*) 75. In the insert: dependence of the maximal temperature $T_m$ under the conditions of restricted heat exchange, [AIBN] = $1.1\times10^{-2}$ M.

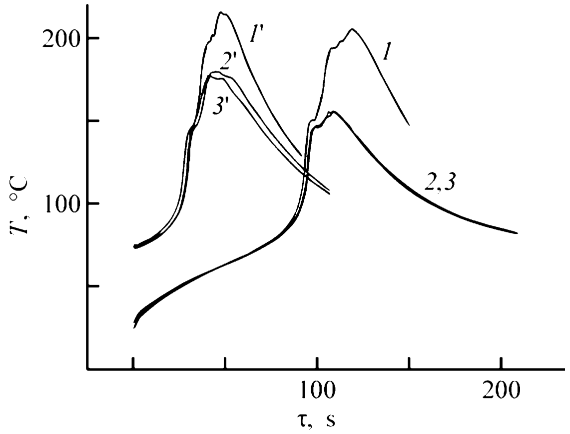


**Fig. 5.** Temperature curves of styrene polymerization in glass ampules in the mode of restricted heat exchange (*1*, *1*') without additives and in the presence of (*2*) urethane U-**IIIb**, (*3*) inhibiting composition based on urethane U-**IIIb**, (*2*') urethane U-**IIc**, (*3*') inhibiting composition based on urethane U-**IIc**. $T_0$ = 75°C, [AIBN] = $2.2\times10^{-2}$ M, [U] = [BuOH] = $2\times10^{-2}$ M, [DBTDL] = $10^{-5}$ M. (*1*'–*3*') Reaction mixture before experiment was rapidly heated to 75°C; (*1*–*3*) initial temperature of the reaction mixture was 20°C.

merization reduce the polymer MW and this effect is the most pronounced for polymerization at elevated temperatures. At 125°C, the effect of the dormant inhibitors on $M_n$ of the resulting polystyrene is significantly weaker as compared to the initial inhibitors, and at 60°C they cause even a slight increase in the polymer molecular weight.

Thus, our experimental data on styrene polymerization under isothermal conditions suggest that urethanes U-**Id**, U-**IIc**, U-**IIe**, U-**IIf**, and U-**IIIa** or their mixtures with alcohol and a catalyst of exchange reactions can be promising DIs. However, the effect of DI can be demonstrated only in the experiments simulating uncontrollable transition of the polymerization process to the high-temperature mode.

Under the conditions of restricted heat exchange, initiated polymerization of styrene can proceed in three different modes, depending on the initial conditions. At a coolant temperature $T_0$ lower than a certain critical value, the process occurs in the low-temperature mode at which the difference between the temperatures of the reaction mixture and thermostat, $T - T_0$, is small and the temperature curve exhibits a flat maximum. At $T_0$ higher than the critical temperature, $T - T_0$ rapidly increases to tens degrees and the temperature curve is characterized by a sharp maximum. Rapid decrease in the temperature after passing the maximum is due to the consumption of the initiator and termination of initiation. This is the mode of high-temperature initiated polymerization. However, if the temperature in the reactor reaches the values providing relatively rapid thermal initiation of polymerization, the system can pass into the high-temperature mode of thermal initiation.

The thermal curves of styrene polymerization, recorded using sealed glass ampules at various $T_0$ on the installation with restricted heat exchange, are shown in Fig. 4. All the three modes are observed in this figure: low-temperature mode ($T_0$ 59.0 and 60.5°C), high-temperature mode of initiated polymerization ($T_0$ 62, 65, and 70°C), and high-temperature mode of thermal polymerization ($T_0$ 75°C). The dependence of the maximal temperature in the ampule on $T_0$, which is shown in the inset, indicates that transition from one mode to another occurs in a narrow $T_0$ range, especially in the region of thermally initiated polymerization.

The effect of DI on the styrene polymerization was studied under the conditions nearly critical ($T_0$ 75°C). As can be seen from Fig. 5 (curves *1*' and *2*', *3*'), which illustrates the typical results of the experiments on the effect of DI on polymerization of styrene under conditions of an uncontrollable reaction, addition of the inhibiting formulation based on urethane U-**IIc** appreciably depresses the temperature of maximal overheating of the reaction mixture in the step of thermal polymerization and does not noticeably affect the process at lower temperatures. In this case, the degree of polymerization is significantly smaller in the presence of DI than that in its absence and the reaction mixture remains fairly fluid.

A similar behavior was observed for the inhibiting formulation based on urethane U-**IIe**. As can be seen, the kinetics of polymerization in the presence of this formulation is close to the kinetics of uninhibited polymerization at temperatures of up to 145°C. At higher temperature, polymerization sharply decelerates and the maximal temperature in the reactor decreases by 35° as compared to the uninhibited process.

Under the nonisothermal conditions, the highest performance is exhibited by urethane U-**IIIb**, which lowers the maximal temperature in the reactor by 50° at a concentration of 0.02 M as compared to the control experiment. At the same time, up to transition to the high-temperature mode, this urethane does not noticeably affect the reaction rate. Additions of BuOH and DBTDL do not appreciably affect the inhibiting activity of this DI (Fig. 5, curves *2* and *3*).

The data on the effect of the urethane-type DI on styrene polymerization, determined under the conditions of restricted heat exchange using glass ampules, were qualitatively confirmed by the experiments carried out in 1- and 8-l metallic reactors equipped with stirrers. The reactors were modified so as to provide the minimal ratio of the heat exchange surface to the volume of the reaction mixture, which allowed us to find the conditions at which the initiated polymerization passes to the high-temperature mode.

Initially we found that, at a constant coolant temperature of 90°C, the system passes to the high-temperature mode as the temperature of the reaction mixture increases to 140–150°C. However, further passing to the high-temperature mode of thermal initiation (similar to that in glass ampules) was not observed. This is probably due to a sharp increase in the heat loss through the nonthermostated inlet for the stirrer in the reaction lid. Hence, it is impossible to evaluate the DI performance under these conditions. As a result, the thermal mode of the process was changed so that after attainment of 90°C in the reactor, the temperature of the thermostat was switched to 120°C. In this case, the system passed to the high-temperature mode of thermal polymerization of styrene as the temperature of the reaction mixture increased to more than 200°C (Fig. 6, curve *1*). As a result, the degree of the monomer conversion was close to unity and the resulting mass could be unloaded from the reactor.

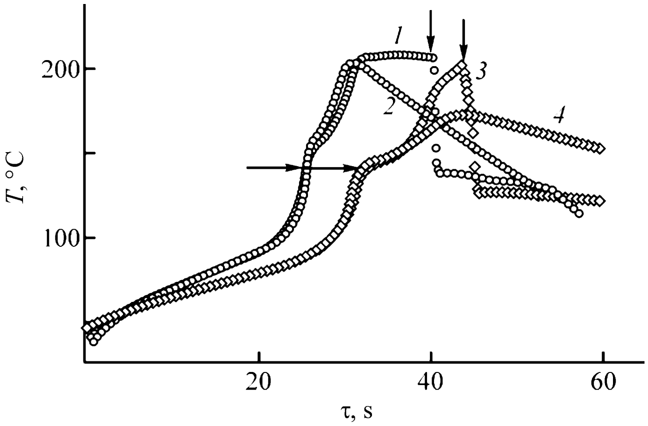


**Fig. 6.** Temperature curves of styrene polymerization in a 1-l metallic reactor (*1*) without additives and (*2*) in the presence of urethane U-**IIIb**, and in an 8-l metallic reactor (*3*) without additives and (*4*) in the presence of an inhibiting formulation based on urethane U-**IIIa**. (*1*, *2*) [AIBN] = $2.2 \times 10^{-2}$ M, (2) [U] = $1.4 \times 10^{-2}$ M; (*3*, *4*) [DIA] = $2 \times 10^{-2}$ M, (*4*) [U] = [BuOH] = $1.5 \times 10^{-2}$ M, [DBTDL] = $10^{-5}$ M. Amount of the monomer loaded, ml: (*1*, *2*) 500 and (*3*, *4*) 5000. Moments of the addition of the cold solvent in the control experiments are shown by the arrows.

Under the same conditions, we performed experiments with DI additives that were tested previously using glass ampules (Fig. 6, curve *2*). As can be seen, urethane U-**IIIb** is less efficient under the given conditions than in the case of the ampule experiments. In its presence, the rate of thermal polymerization even somewhat increases as compared to the control experiment. However, even in this case, the temperature maximum is lower by 5° than that in the control experiment, and, after attainment of the maximum, the temperature of the reaction mixture sharply decreases and the polymerization virtually terminates. The final product is fluid, and it can be discharged from the reactor without dilution with a solvent, as in the control experiment.

The results obtained for a 1-l reactor were taken into account when choosing the process modes of styrene polymerization in an 8-l reactor. This reactor was also modified to diminish the heat exchange in order to provide the possibility of attainment of the high-temperature mode of thermal polymerization. In these experiments, the temperature control unit of the thermostat was switched from 90 to 120°C when the temperature of the reaction mixture reached 150°C. The thermal modes in the course of styrene polymerization in an 8-l reactor are shown in Fig. 6 (curves *3*, *4*).

In the control experiment, when the temperature in the reactor exceeded 200°C, cold xylene was poured to lower the temperature of the reaction mixture and to prevent uncontrollable emergency situation. Otherwise, the stirrer could be blocked and it could become impossible to unload the reaction mixture from the reactor because of the high viscosity at a conversion close to 100%. In the experiments with addition of the inhibiting formulation based on U-**IIIa**, the maximal temperature decreased by no less than 30° as compared to the control experiment, especially if we take into account that the control experiment was terminated at the temperature of the reaction mixture of 202°C, before the maximal temperature was attained.

## CONCLUSIONS

(1) Dormant inhibitors of the urethane type (phenolic inhibitors blocked with isocyanates) prevent uncontrollable emergency situations in the course of styrene polymerization.

(2) In the presence of dormant inhibitors, the maximal temperature in the reactor strongly decreases and the resulting reaction mixture is a viscous mass at a conversion of about 75%, whereas in their absence the conversion reaches almost 100%.

(3) The performance of dormant inhibitors of the urethane type can be controlled by addition of proton-donor compounds accelerating liberation of the phenol inhibitor from urethane at elevated temperatures. The majority of urethanes tested do not significantly affect both the kinetics of low-temperature polymerization and the molecular-weight characteristics of the resulting polymer.

## ACKNOWLEDGMENTS

The study was financially supported by the International Science and Technology Center (project no. 1529).

## REFERENCES

1. Biesenberger, J.A. and Sebastian, D.H., *Principles of Polymerization Engineering*, New York: Wiley, 1983. Translated under the title *Inzhenernye problemy sinteza polimerov*, Malkin, A.Ya., Ed., Moscow: Khimiya, 1988.
2. USSR Inventor’s Certificate, no. 209 742.
3. *Vinyl Polymerization*, Ham, G., Ed., New York: Dekker, 1972.
4. *Handbook of Radical Polymerization*, Matyjaszewski, K. and Davis, T.P., Eds., New York: Wiley, 2002.
5. Simonyi, M., Fitos, I., Kardos, J., et al., *J. Chem. Soc., Faraday Trans. 1*, 1977, vol. 73, no. 9, p. 1285.
6. Badamshina, E.R. and Gafurova, M.P., *Vysokomol. Soedin., Ser. C*, 2002, vol. 44, no. 9, pp. 1643-1659.
7. RF Patent 2 277 104.
8. Edel’shtein, O.A., *Cand. Sci. Dissertation*, Irkutsk, 1972.
9. Korolev, G.V. and Perepelitsina, E.O., *Vysokomol. Soedin., Ser. B*, 1977, vol. 39, no. 2, p. 338.
10. Kuzaev, A.I., *Vysokomol. Soedin., Ser. A*, 1980, vol. 22, no. 5, pp. 1146–1151.
11. Korolev, G.V., Grachev, V.P., Irzhak, V.I., et al., Abstracts of Papers, *Tret’ya Vserossiiskaya Karginskaya konferentsiya “Polimery-2004”* (3rd All-Russia Kargin Conf. “Polymers-2004”), Moscow: Mosk. Gos. Univ., 2004, vol. 2, p. 18.
12. Korolev, G.V., Grachov, V.P., Irzhak, V.I., et al., Abstracts of Papers, *40th Int. Symp. on Macromolecules “Macro-2004,”* July 4–9, 2004, p. 73.
13. Romankov, P.G. and Frolov, V.F., *Teploobmennye protsessy khimicheskoi tekhnologii* (Heat Exchange Processes of Chemical Technology), Leningrad: Khimiya, 1982.
14. Dzhalmukhanova, A.S., Badamshina, E.R., Komratova, V.V., et al., *Kinet. Katal.*, 2008, vol. 49, no. 1, pp. 57–63.