ISSN 1560-0904, Polymer Science, Series B, 2017, Vol. 59, No. 2, pp. 216–224. © Pleiades Publishing, Ltd., 2017.
Original Russian Text ©A.S. Shabaev, A.A. Zhansitov, Zh.I. Kurdanova, S.Yu. Khashirova, A.K. Mikitaev, 2017, published in Vysokomolekulyarnye Soedineniya, Seriya B, 2017, Vol. 59, No. 2, pp. 168–176.

INVESTIGATION METHODS

New Method of Investigation of Polysulfone Thermal Destruction

A. S. Shabaev, A. A. Zhansitov, Zh. I. Kurdanova, S. Yu. Khashirova*, and A. K. Mikitaev

Kabardino-Balkar State University, ul. Chernyshevskogo 173, Nalchik, 360004 Russia

** e-mail: new_kompozit@mail.ru*

Received July 6, 2016;
Revised Manuscript Received November 17, 2016

Abstract—The regularities of branching and thermal destruction processes of polysulfones of different chemical structure at 150–500°C are studied depending on the nature of the reactive medium and blocking method of the terminal groups with the use of a special device for a gas chromatograph allowing one to investigate the branching and thermal destruction of polymers. It is found that the nature of the solvent and deactivator of the terminal hydroxyl groups substantially affects the crosslinking and destruction processes of polysulfones.

DOI: 10.1134/S1560090417020099

The distinctive feature of the whole series of the polysulfones is their high fire resistance, low density of fume emission, chemical stability in a lot of aggressive media and solvents, high temperature of long-term operation (up to 250°C), and good physicomechanical properties. The most significant fields of their application are electronics, the aerospace industry, transport engineering, and biomedical engineering and as matrices for 3D printing.

The problems connected with the chemical transformations of polysulfones at high temperatures (over 400°C) not only are of theoretical interest but also have practical significance in revealing the destruction mechanisms of polysulfones during processing and operation.

The thermal stability of polysulfones is poorly explored [1–9]. Nevertheless, it is known that from 400°C the polysulfone decomposition is accompanied by SO_2 release. In this case, among the liquid products, phenol is formed. Later, some authors [10–12] found that there were almost no volatile products at lower temperatures, but the polysulfone structuring was observed. The latter depends on the initial polymer structure. The heating of polysulfones in the temperature range of 400–500°C leads to release of H_2, CO, CH_4, CO_2, and SO_2.

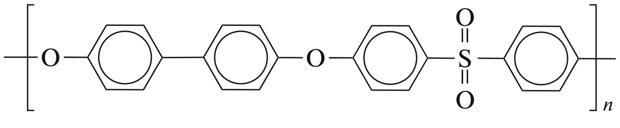
The thermal destruction of polysulfones below 300°C has hardly been studied. All the more, the effects of the synthesis method, terminal group structure, and purification and drying methods of the polymer material on their thermal and physicomechanical properties have not been explored.

In this connection, the purpose of the present work consisted in investigation of the crosslinking and destruction processes of polysulfones of different chemical structure at 150–500°C depending on the production and terminal group blocking methods using a specially developed device for a gas chromatograph.

EXPERIMENTAL

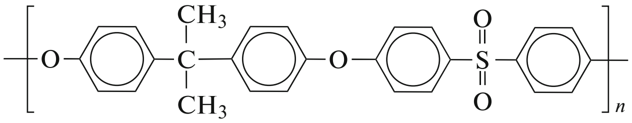
The polysulfones synthesized in the laboratory of progressive polymers of Kabardino-Balkar State University with the characteristic viscosity of 0.5 dL/g were the objects of investigation. The thermogravimetric investigations were carried out on a TGA 4000 derivatograph (PerkinElmer) in air and nitrogen atmosphere. The temperature rise rate was 5 K/min over the range of 30–750°C.

The polymer was synthesized by a high-temperature polycondensation by the nucleophilic substitution method using as the initial monomers 4,4'-dihydroxudiphenyl, 4,4'-dioxydiphenyl-2,2'-propane, 4,4'-difluorodiphenylketone, 4,4'- dioxyphthalophenon, 4,4'-dichlorodiphenylsulfone, and potassium carbonate (alkaline agent) in a medium of aprotic-dipolar solvent (DMAA or DMSO). In the case of polyphenylenesulfone



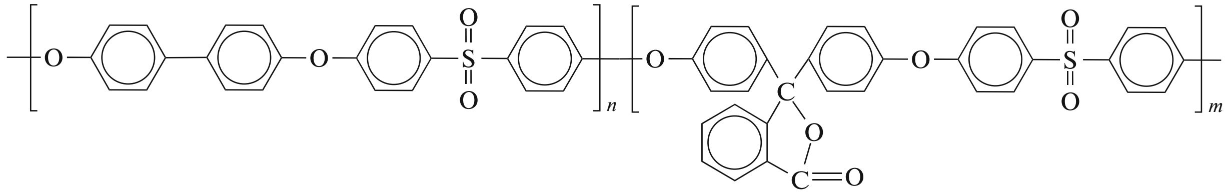
I

and polysulfone

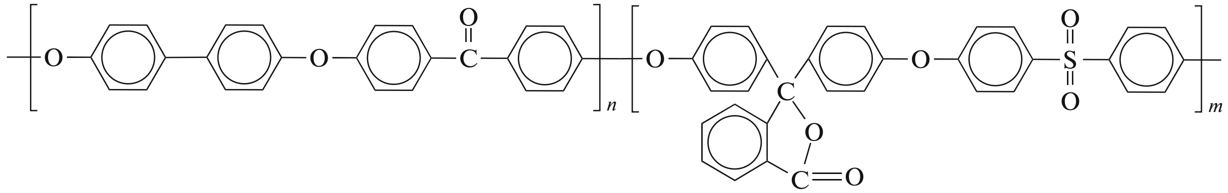


IV

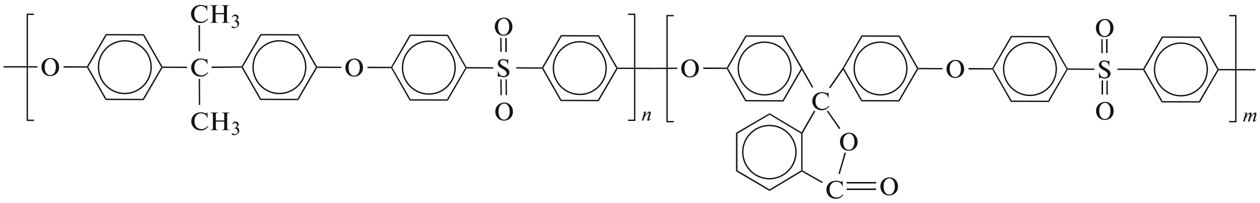
the initial monomers were taken in equimolar amount. Copolymers



II



III



V

were synthesized at the ratio of 4,4'-dihydroxydiphenyl or 4,4'-dioxydiphenyl-2,2'-propane and/or 4,4'-difluorodiphenylketone monomers to phenolphthalein of 4 : 1. Both homo- and copolymers were synthesized under similar conditions for 3 h after the removal of water from the reaction system. The blocking of the terminal groups was performed by the excess of the halogen-containing monomer or introduction of acetylchloride into the reaction mixture at the end of synthesis.

The reduced viscosity of the obtained polymers (0.5% solution in DMAA at 25°C) was determined after drying in vacuum at 100, 150, and 200°C.

The crosslinking and thermal stability of polysulfones were investigated using a Tsvet-800 gas chromatograph with a thermal conductivity detector and absorption column with length of 5 m filled with polysorb-1, impregnated with 5% solution of polyethyleneglycoladipinate. The content of H_2, CO, CH_4, CO_2, and SO_2 was analyzed under the following conditions of the chromatographic procedure: volume flow of argon carrier gas of 30 mL/min; detector temperature of 160°C; evaporator temperature of 100°C; column thermostat temperature of 100°C; detector current of 80 mA.

In order to perform the pyrolysis of samples, a special attachment was constructed and produced, and the scheme of feeding of the polymer decomposition products into chromatograph was created (Fig. 1). This device differs from existing ones in that it has a third gas line allowing one to feed to the working chamber by choice the carrier gas, oxygen, or air with different degree of humidity. In addition, the scheme provides a cooling chamber to select the liquid products of the polymer decomposition with the aim to analyze them by an IR spectroscopy method. The hydraulic seal at the end of this line allows one to investigate the polymer decomposition processes in both open and closed systems.

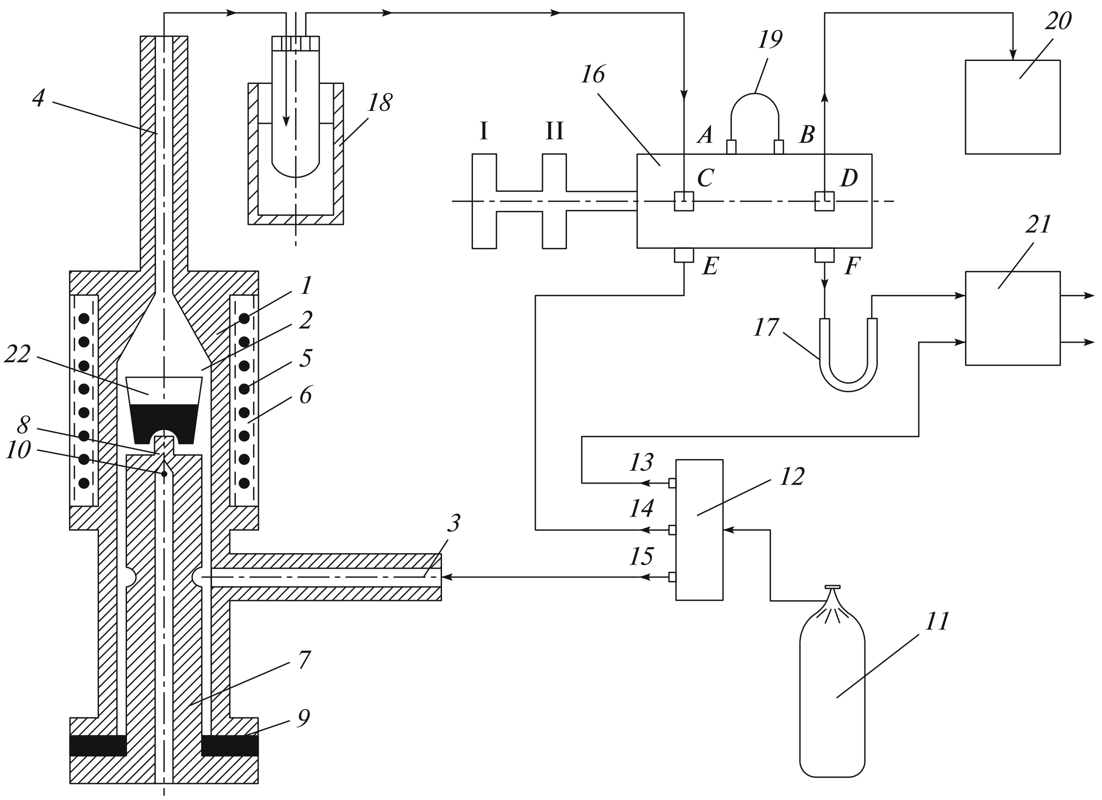


Fig. 1. Special attachment for gas chromatograph. (*1*) Pyrolytic cell, (*2*) working chamber, (*3*, *4*) input and output channels for gas supply, (*5*) heating element, (*6*) heat-insulating layer, (*7*) closure fitting with a crucible holder (*8*), (*9*) joint sealing insert, (*10*) controlling thermocouple, (*11*) gas tank, (*12*) block of gas preparation, (*13*, *14*) gas lines of chromatograph, (*15*) third gas line feeds gas into cell chamber, (*16*) six-port sample valve, (*17*) separating column, (*18*) cooling chamber, (*19*) dispensing loop, (*20*) hydraulic seal, (*21*) analytic unit of chromatograph, (*22*) crucible with the sample.

The samples were heated at the rate of 50 K/min rate under a closed hydraulic seal.

RESULTS AND DISCUSSION

The drying of polysulfones I–V at temperatures from 150 to 200°C leads to a rise in the reduced viscosity; for example, for polysulfone I, it rises by 25% in 3 h. Such behavior indicates the chemical modification of polysulfones before their processing into articles, which leads to deterioration of physicomechanical properties and processability.

Some authors [10–13] previously found that, at relatively low temperatures, the terminal phenoxy groups of polysulfones are added to the phenylene fragment of the chain. This results in the splitting of a hydrogen atom from the phenyl ring, which promotes their crosslinking. At higher temperatures, such reaction ends almost always in decomposition of the main polymer chain. In this connection, it was interesting to investigate the crosslinking of polysulfones by the hydrogen release depending on their chemical structure and the methods of synthesis and blocking of the terminal hydroxyl groups.

Polysulfone with the structural unit I was produced under the following conditions: in the presence of DMSO without the blocking of the terminal groups (Ia) and in DMAA with the blocking of the terminal groups by dichlorodiphenylsulfone.

Polysulfone with the structural unit II was synthesized in DMSO with the blocking of the terminal groups by acetylchloride (IIa), in DMAA with the blocking of the terminal groups by acetylchloride (IIb), and in DMAA with the blocking of the terminal groups by dichlorodiphenylsulfone (IIc). The percentage of polyphenylensulfone and phenolphthalein in polysulfone II was 75 : 25, respectively.

Polysulfone III was produced in DMAA with the blocking of the terminal groups by dichlorodiphenylsulfone. The percentage of polyphenylensulfone and phenolphthalein was 75 : 25.

Polysulfone IV was obtained in DMAA with the blocking of the terminal groups by dichlorodiphenylsulfone.

Polysulfone V was produced in DMAA with the blocking of the terminal groups by dichlorodiphenyl-

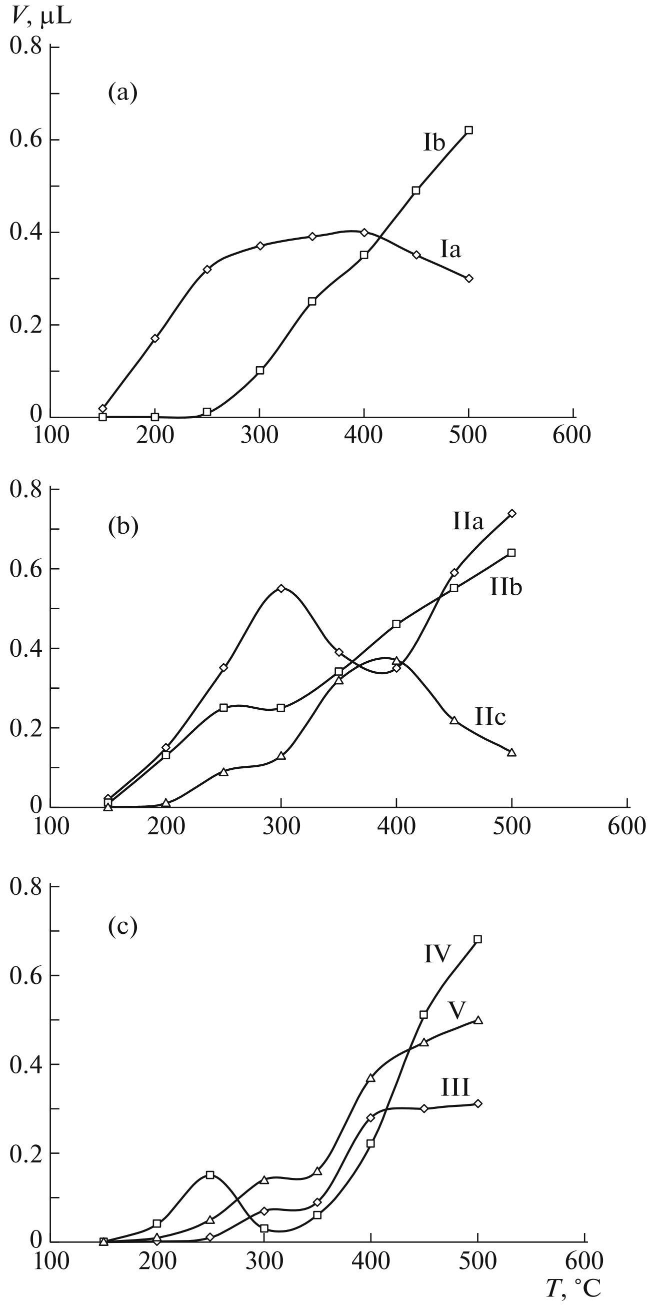


Fig. 2. Kinetic curves of hydrogen release for polysulfone I (a), II (b), and III, IV, and V (c).

sulfone. The percentage of polysulfone and phenolphthalein was 75 : 25.

Figure 2 shows the kinetic curves of hydrogen release for all polymers listed above at 150–500°C. The thermostating time was 60 min for each point; the specimen was 100 mg.

At the first stage, we managed to find out the influence of the aprotic-dipolar solvent used in synthesis of polysulfones on the crosslinking and destruction. For polysulfone Ia, the beginning of the hydrogen release corresponds to 150°C; its yield rises constantly with the rise in temperature up to 400°C, and for polysulfone Ib, its formation is fixed at 250°C (Fig. 2a). This is explained by the destructing effect of DMSO impurities on polysulfone; such changes become catastrophic at DMSO content over 0.5 wt %.

If one judges by C–S bond strength in DMSO (264 kJ/mol) and the greater total reactivity of sulfoxides compared to sulfones, DMSO is thermally instable. There is molecular thermal *cis*-splitting with olefin formation at low temperatures (about 100°C), although the hemolytic breaking of C–S bond at higher temperatures is assumed. During the polysulfone processing, the DMSO residues play the role of a peculiar radical initiator of destruction [14].

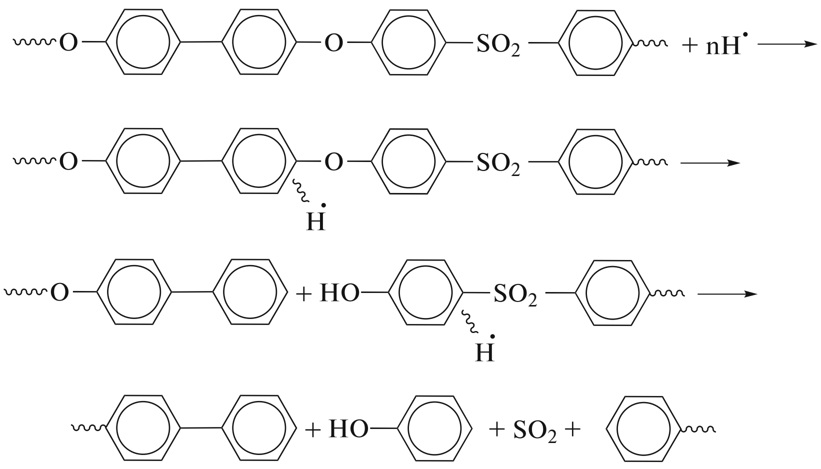
The indirect confirmation of the fact that polysulfone Ia is more crosslinked than polysulfone Ib is the amount of formed hydrogen at temperatures over 400°C. Its sharp rise for polymer Ib compared to polymer Ia indicates that the active hydrogen atom takes part in decomposition of the main chain in more crosslinked structures, which leads to a decrease in its release.

The kinetic curves of the hydrogen release for copolymers IIa, IIb, and IIc are presented in Fig. 2b.

For copolymers IIa and IIb, the terminal groups of which are blocked by acetylchloride, the beginning of the hydrogen release is observed at the same temperature (150°C). For copolymer IIc, the hydroxyl groups are blocked by dichlorodiphenylsulfone. This leads to a rise in the temperature of the beginning of the hydrogen release. It is evident that an important factor determining the crosslinking and destruction processes of polysulfone is a good choice of the aprotic-dipolar solvent (DMAA) and deactivator of the terminal hydroxyl groups (dichlorodiphenylsulfone).

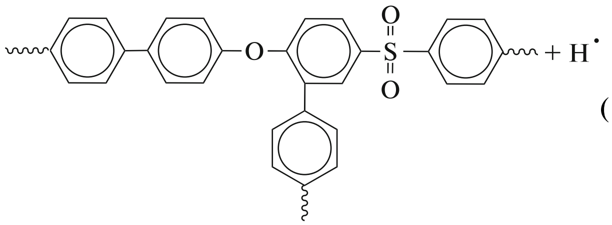
Using these data, we synthesized the copolymers III, IV, and V. As was expected, the hydrogen release for all copolymers decreased substantially and shifted to higher temperatures (Fig. 2c).

Somewhat unusual shape of the hydrogen release curves for polymers IIb and IIc (Fig. 2c) and S-shape of curves III and V (Fig. 2c) are connected with the fact that the hydraulic seal is closed at the sample pyrolysis (Fig. 1). Such a pyrolysis system is called closed, and all decomposition products contact the sample. Therefore, the forming atomic hydrogen during the polymer crosslinking participates in the reaction with the main polymer chain, which leads to its consumption and decomposition of the main polymer chain:



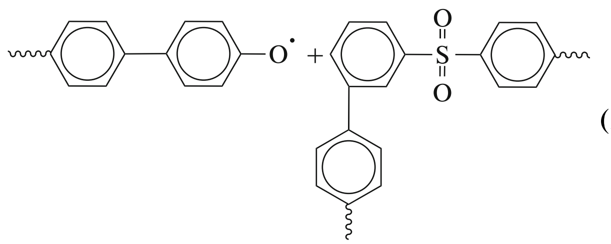
The further rise in the pyrolysis temperature (400–500°C) leads to the increase in the registered hydrogen (Fig. 2c) thanks to the emergence of new sources of its formation (decomposition of benzene ring, coke-formation, etc.).

Thus, on the basis of the investigations of the polysulfone structural transformations at the processing temperatures by the gas chromatography method, we managed to select the synthesis conditions of polymers and find the optimal variant of the blocking of the terminal hydroxyl groups with the aim to eliminate the premature crosslinking of polysulfones. The results allowed us to establish that the polysulfones can decompose in two directions. In the first case, the crosslinking of the polymer chains occurs with the release of atomic hydrogen:



(1)

In the second case, the main chain is broken. In our case, the transformations occur mainly by scheme (1):

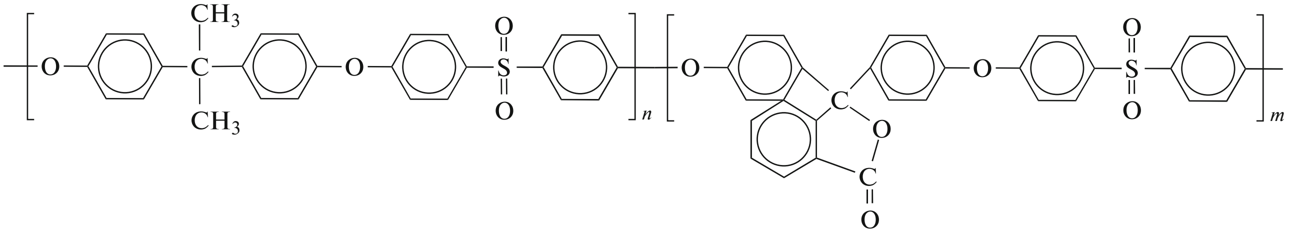


(2)

It was of interest to investigate the dependence of the thermostability of polysulfones and their copolymers on the chemical structure at higher destruction temperatures. Figure 3 illustrates the thermogravimetric curves of polymers in air and an inert medium. The polysulfones synthesized in DMAA with the terminal hydroxyl groups blocked by dichlorodiphenylsulfone were chosen.

The beginning of the mass loss in air for all polymers lies in the interval of 420–490°C, where the polymers with diane fragments (polymers IV and V) are less thermostable. In the inert medium, the temperatures at the beginning of the mass loss are shifted to 450–500°C, where the same polymers are less thermostable. Let us note that, in the absence of oxygen, the decomposition of polymers proceeds in one stage with the formation of coke residues in the range of 30–40% of the mass of the samples under investigation. The mass loss curves have two expressed stages in air (Fig. 3a). The first stage corresponds to reactions of the main polymer chain breaking, the rate of which points to the radical-chain mechanism of their destruction. At the second stage, the rate of mass loss clearly decreases, which indicates the transition of the radical-chain mechanism into the simple combustion reactions.

In order to judge in detail the character of the processes in polysulfones at 400–500°C, we explored the regularities of formation of the main gaseous products forming at the thermal decomposition of polymers. The object of investigation was polysulfone synthesized in DMAA with the blocking of the terminal hydroxyl groups by dichlorodiphenylsulfone of the following structure:



This polymer contains 25% of phenolphthalein fragment per total mass of copolymer. The preliminary investigations showed that the main gaseous products of the polymer thermal destruction at 400–500°C are CO, CO_2, H_2, CH_4, and SO_2.

The formation of these products was analyzed in the isothermal modes at 400, 425, 450, 475, and 500°C and thermostating time up to 100 min.

Figure 4 shows the kinetic curves of CO, CO_2, H_2, CH_4, SO_2 release. The analysis of the kinetic curves of release of the main gaseous products at the thermal destruction of the polymer under investigation showed that CO and CO_2 are most intensely formed at 400 and 425°C (Figs. 4a, 4b); their source can be only the phthalide group in the phenolphthalein fragment; i.e., as in the case of polyarylates containing these groups [15], the decomposition of the polysulfone under

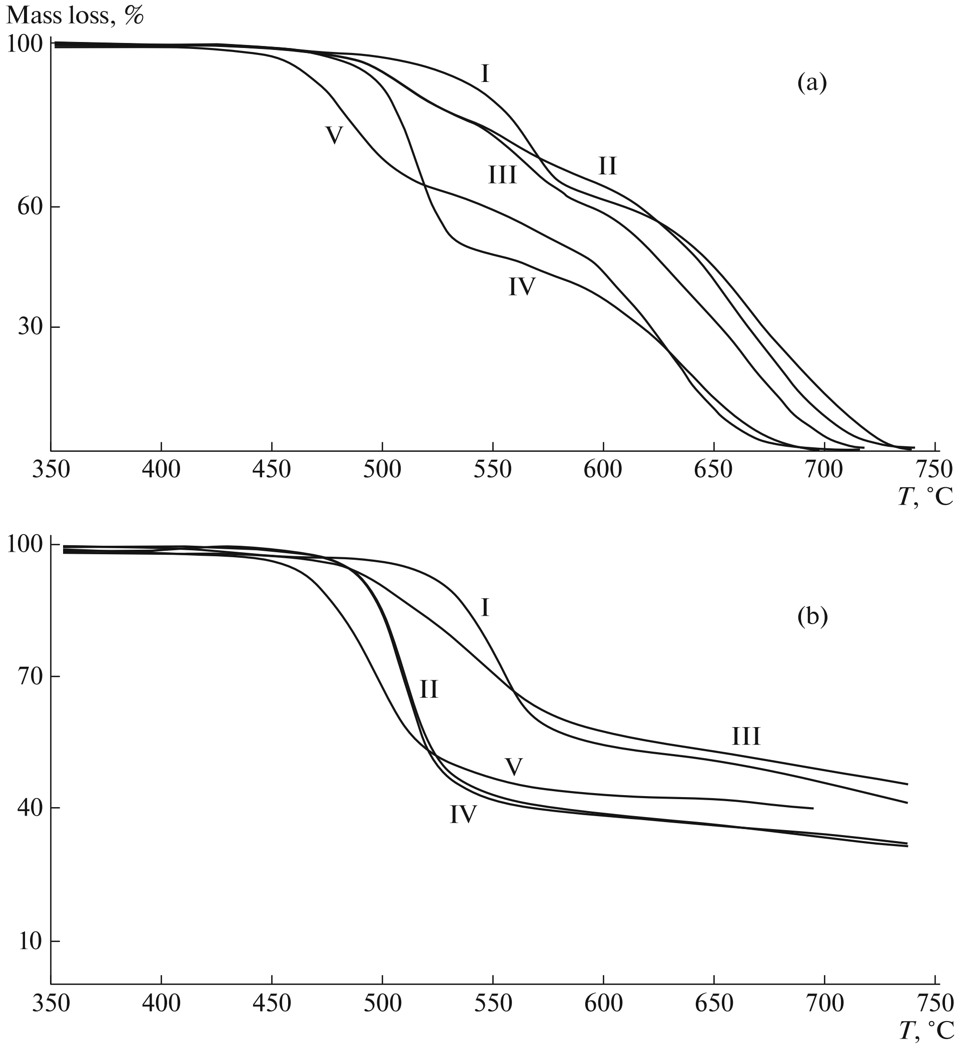
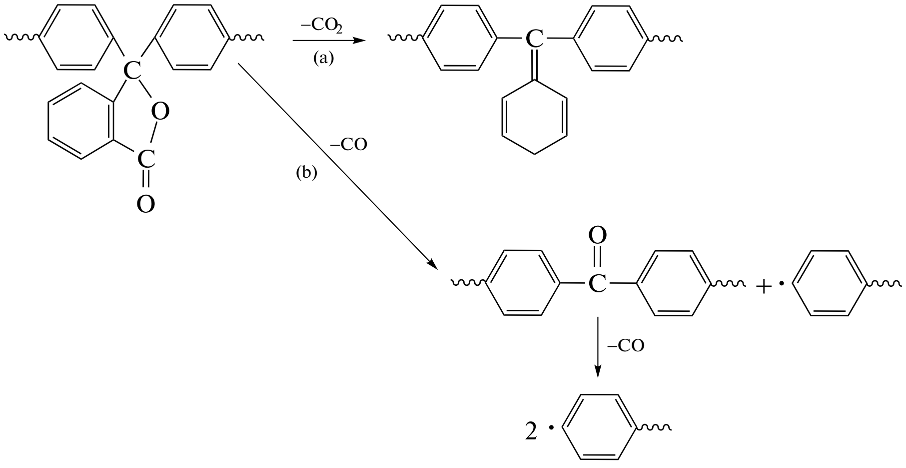


Fig. 3. Thermogravimetric curves of mass loss in air (a) and inert medium (b) for polysulfones I–V.

investigation begins from the decomposition of phenolphthalein fragment. A general regularity of the kinetic curves of CO_2 formation is a decrease in its amount at 450, 475, and 500°C, accompanied by a sharp rise in CO yield at the same temperatures. Such phenomenon allowed us to conclude that the phenolphthalein fragment decomposes by different mechanisms depending on temperature:



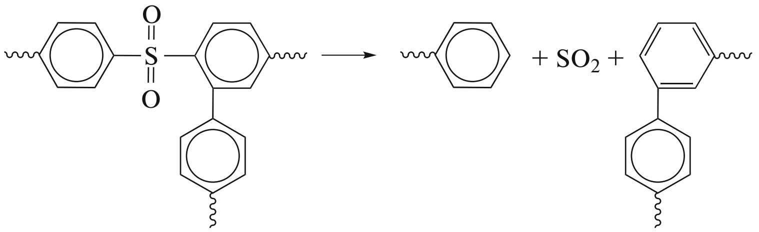
At 400–425°C, the phthalide group decomposes mainly by mechanism *a* with CO_2 release. At higher temperatures (450–500°C), it decomposes mainly by mechanism *b* with formation of CO and phenyl radicals, capable of further participation in the polymer decomposition.

Apart from the products mentioned above, at the decomposition of polysulfone, methane and hydrogen are formed in significant amounts (Figs. 4c, 4d), the content of which in the decomposition products increases noticeably with the rise in temperature and thermostating time. The hydrogen release at 400–450°C is connected with the crosslinking of the polymer chains observed at relatively low temperatures. At higher temperatures (475–500°C), the hydrogen source is phenylene fragments; their decomposition is accompanied by coke formation.

The presence of methane in the pyrolysis products indicates the detachment of methyl groups from the isopropylidene bridge with subsequent addition of atomic hydrogen to them. In this case, such reaction is noticeable from 425°C.

Some authors [16–21] during the investigation of the thermal destruction of polysulfones of different structure showed that their decomposition at a noticeable rate occurs as a result of breaking of the C–S bonds of the polymer chain, as the weakest at temperatures exceeding 400°C, and SO_2 is the main gaseous product of destruction.

The investigations of the present work demonstrate that the formation of sulfur dioxide begins at 450°C and above (Fig. 4e). This fact is probably connected with the good selection of the aprotic-dipolar solvent and deactivator of the terminal hydroxyl groups during the polysulfone synthesis, which made it possible to avoid early crosslinking of polymers, which is always accompanied by active hydrogen atom release. Thus, the breaking of the C–S bond occurs through addition of the phenyl radicals to the main chain, which are formed abundantly at the decomposition of the phthalide groups of the phenolphthalein fragments:



One could assume that the sulfur dioxide is released at lower temperatures and it is instantaneously reduced to hydrogen sulfide by hydrogen. These reactions were observed in [10]. However, there were no noticeable amounts of hydrogen sulfide at all temperatures.

Thus, a new method of investigation of polymer crosslinking using a gas chromatograph was devel-

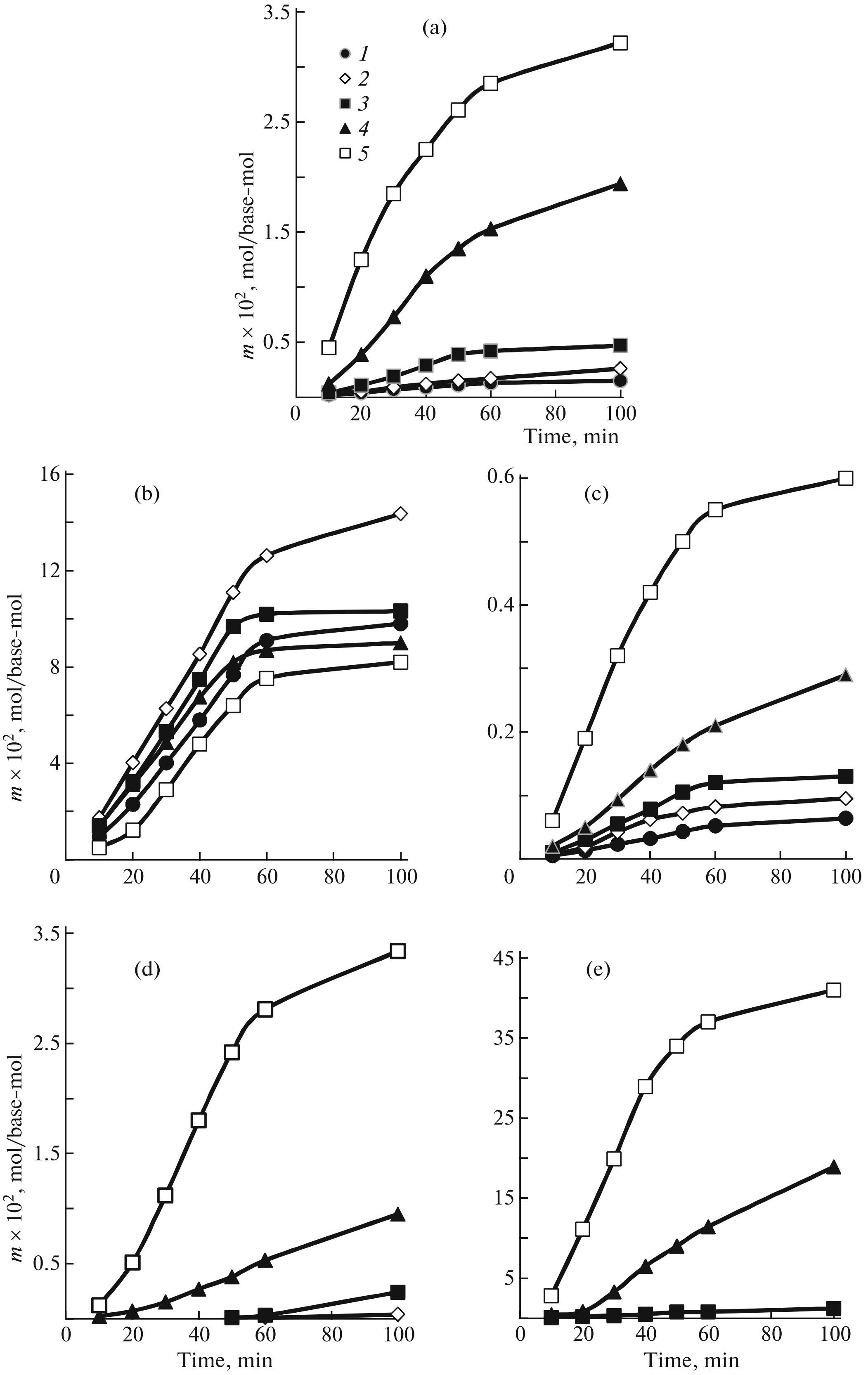


Fig. 4. Kinetic curves of release of CO (a), CO_2 (b), H_2 (c), CH_4 (d), and SO_2 (e). T = 400 (*1*), 425 (*2*), 450 (*3*), 475 (*4*), and 500°C (*5*).

oped. A new device for investigation of the polymer thermal transformations in a wide temperature range (150–800°C) was proposed. The investigations showed that the decrease in the polysuflone crosslinking at temperatures from 150 to 300°C requires the blocking of the terminal hydroxyl groups by dichlorodiphenylsulfone.

REFERENCES

1. E. M. Fettes and F. O. Devis, “Polysulfones. Polyethers,” in *High Polymers*, Ed. by N. G. Gaylord (Interscience Publ., New York, 1962), Vol. 13, p. 249.
2. R. Gabler, Chimia **28**, 567 (1974).
3. M. E. A. Cudby, R. G. Feasey, B. E. Jenninges, M. E. B. Jones, and J. B. Rose, Polymer **6**, 589 (1965).
4. H. A. Vogel, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) **10**, 160 (1969).
5. W. F. Hale, A. G. Farnham, R. N. Johnson, and R. A. Clendinning, J. Polym. Sci., Part A: Polym. Chem. **5**, 2399 (1967).
6. A. K. Mikitaev, V. V. Korshak, and G. B. Shustov, Vysokomol. Soedin., Ser. A **24**, 2558 (1982).
7. I. P. Storozhuk, L. B. Shirokova, P. M. Valetskii, L. Z. Rogovina, G. G. Nikiforova, S. V. Vinogradova, V. V. Korshak, and G. L. Slonimskii, Vysokomol. Soedin., Ser. A **21**, 152 (1979).
8. L. H. Perng, J. Polym. Sci., Part A: Polym. Chem. **38**, 583 (2000).
9. L. H. Perng, J. Appl. Polym. Sci. **81**, 2387 (2001).
10. L. I. Danilina, E. N. Teleshov, and A. N. Pravednikov, Vysokomol. Soedin., Ser. A **16**, 581 (1974).
11. L. I. Danilina, E. N. Teleshov, and A. N. Pravednikov, Dokl. Akad. Nauk SSSR **207**, 1121 (1972).
12. L. I. Danilina, V. N. Muromtsev, and A. N. Pravednikov, Vysokomol. Soedin., Ser. A **17**, 2592 (1975).
13. R. Z. Magaril, *Mechanism and Kinetics of Homogeneous Thermal Transformations of Hydrocarbons* (Khimiya, Moscow, 1970).
14. E. V. Kalugina, Doctoral Dissertation in Chemistry (ICP RAS, Moscow, 2003).
15. V. V. Rode, I. V. Zhuravleva, S. R. Rafikov, V. V. Korshak, S. V. Vinogradova, and S. N. Salazkin, Vysokomol. Soedin., Ser. A **6**, 994 (1964).
16. V. N. Shelgaev, A. S. Shabaev, and A. K. Mikitaev, Vysokomol. Soedin., Ser. A **24**, 2315 (1982).
17. H. M. Tarnowicki, Mitt. Chem. Forschunginst. Wirtsch. Oesterr. **24**, 296 (1970).
18. A. Devis, Makromol. Chem. **128**, 242 (1969).
19. V. N. Shelgaev, M. M. Gazaev, A. S. Shabaev, G. E. Zaikov, and A. K. Mikitaev, Plast. Massy, No. 1, 45 (2011).
20. I. I. Levantovskaya, G. V. Dralyuk, O. A. Mochalova, I. A. Yurkova, M. S. Akutin, and B. M. Kovarskaya, Vysokomol. Soedin., Ser. A **13**, 8 (1971).
21. V. N. Shelgaev, M. M. Gazaev, G. E. Zaikov, A. S. Shabaev, M. B. Gokzhaev, A. K. Mikitaev, Plast. Massy, No. **2**, 25 (2011).

Translated by K. Aleksanyan