American Journal of Engineering Research (AJER)
e-ISSN: 2320-0847 p-ISSN : 2320-0936
Volume-12, Issue-05, pp-115-118
www.ajer.org
Article review Open Access

Synthesis and Investigation of Photosensitive Polymer

[1]Mamedli S.B., [2]Chobanova U.F., [1]Isgandarova E.G.,
[1]R.V.Asadov, [3]Jabbarli U.S.

[1]Institute of Polymer Materials of the Ministry of Science and Education of the Republic of Azerbaijan, Sumgait
[2]Azerbaijan State University of Oil and Industry, Baku, Azerbaijan
[3]Institute of Radiation Problems of the Ministry of Science and Education of the Republic of Azerbaijan, Baku, Azerbaijan

ABSTRACT:
The radical copolymerization of styrene with isoprene has been carried out. It is shown that their copolymerization proceeds with the opening of the double bond of the vinyl group of styrene and isoprene. The copolymerization constants have been determined (r_1=2.1, r_2=0.28) and the factors of activity and polarity of the used monomers have been calculated. It is shown that the synthesized copolymers are capable of structuring under action of UV irradiation and exhibit good photosensitive properties (Ψ=53 $cm^2 \cdot J^{-1}$). It has been revealed that the adhesion value for the copolymer of styrene with isoprene is 10 MPa. The molecular weight indices of the copolymer (polystyrene + isoprene) have been determined: $\overline{M}_w = 724500$, $\overline{M}_n = 255500$, $\overline{M}_w/\overline{M}_n$ =2.8.
Keywords: *styrene, isoprene, radical copolymerization, microelectronics, photosensitivity, copolymerization constants, activity, polarity*

Date of Submission: 02-05-2023 Date of acceptance: 12-05-2023

I. INTRODUCTION

In connection with the development of microelectronics, a special attention is paid to the synthesis of new polymers with the aim of improvement of the basic properties of photosensitive polymers [1-7]. The polymers containing double bonds, which are structured under the action of UV rays, are referred to a number of the high-molecular substances exhibiting such properties.

The polymers containing double bonds in their macromolecules are used as reactive compounds and from the point of view of their properties, the synthesis of such polymers and the study of their properties are of great interest [8-13].

In this work, the radical binary polymerization reaction of styrene with an isoprene monomer has been carried out at various molar ratios of monomers, the regularities of the copolymerization reaction have been studied and the photosensitive properties of the obtained copolymer have been determined.

EXPERIMENTAL PART

The radical binary copolymerization reaction of styrene with isoprene was carried out in the presence of the initiator (benzoyl peroxide) in a benzene solution, in an ampoule, at temperature 70°C, in a thermostat. The obtained styrene copolymer with isoprene was purified by double precipitation from benzene solutions with methanol and dried at 30°C in vacuum (15-20 mm mer.c.).

The composition of the obtained copolymer has been established using elemental analysis, and its structure – using spectral methods (IR and NMR) of analysis.

They are well soluble in dimethylformamide, dioxane, etc., but insoluble in low molecular weight alcohols (methanol, ethanol).

The copolymerization constants (r_1 and r_2) of the used monomers were determined on the Feyneman-Ross method.

The characteristic viscosity of the polymer was determined in Ostwald viscometer in a benzene solution at 20°C.

The microstructure parameters of styrene with isoprene were determined using the equation given in [14].

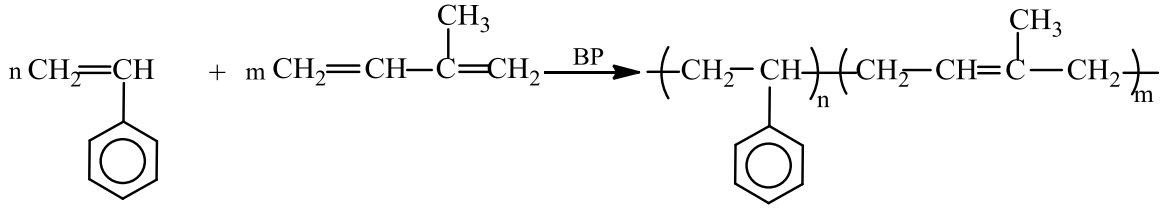
According to the Alfrey-Price Q-e scheme, the activity and polarity of the styrene copolymer with isoprene were calculated.

The molecular-weight parameters of the polymer were determined by a method of gel-permeating chromatography.

For investigation of the photosensitivity of the synthesized copolymer, their 10% solution was prepared and applied to a glass substrate with size of 70×100 mm. The layer was dried for 10 min. For UV irradiation, an Hg lamp DRT-230 (current strength – 2.5 A) was used. In the device, the exposure time – 5-20 s, the distance from the radiation source is 15 cm, and the exponometer shutter rate is 710 mm / h. The insoluble part of the synthesized polymer was determined on the ratio of its mass to the initial film mass.

II. RESULTS AND DISCUSSION

It has been established that the copolymerization reaction proceeds with the opening of the vinyl group in both monomers and a copolymer containing double bonds is formed. The polymerization process proceeds according to the following scheme:



The synthesized copolymers are white substances having different forms depending on their composition.

Under the established optimal conditions, the foreign polymerization reactions, including the formation of cross-linked polymers were practically not observed. These factors are observed both during the release of the formed polymers and during the dissolution of copolymers.

For preparation of more complete information about copolymerization reactions, these reactions were carried out by changing the comonomers at various molar ratios, in a wide range, at low conversion depth (10-12%) and the compositions of the formed copolymers (m_1 and m_2) have been found by means of these reactions. On the basis of the obtained results, the copolymerization constant values (r_1 and r_2) of the used monomers on the Feyneman-Ross method, and also the characteristic viscosity and photosensitivity index of the copolymer synthesized on the basis of styrene and isoprene have been found (Table 1).

Table 1. Conditions of carrying out of the radical binary copolymerization reactions in the styrene+isoprene system and the content of links in the obtained copolymers (solvent – benzene, stimulant – 0.5% benzoyl peroxide, conversion <10%, t=70°C)

№	Quantity of monomers in the initial mixture, mol %		Compositions of copolymers, mol %		Copolymerization constants		Double bond, %	[η] dl/g	Photosensitivity, $cm^2 \cdot C^{-1}$
	M_1	M_2	m_1	m_2	r_1	r_2			
1	10	90	25.57	74.43			2.41	0.92	
2	25	75	47.92	52.08			7.12	–	
3	50	50	72.58	27.42	2.1	0.28	9.85	0.85	
4	75	25	85.43	14.57			14.8	–	53
5	90	10	94.09	5.91			23.65	0.88	

It can be seen from the results presented in Table 1 that the composition of the copolymer strongly depends on the molar composition of the initial mixture of monomers. In the obtained copolymer, the change of the quantity of styrene monomer in the initial mixture in the range of 10-90 mol.% leads to the increase in quantity of styrene links in a copolymer from ~ 25.57 mol.% to 94.09 mol.%. It can be seen from the copolymerization reaction rate constants that the styrene is a more active monomer than isoprene monomer. The activity and polarity of the comonomers were calculated according to the Alfray-Price Q-e scheme (Table 2).

Table 2. Q-e parameters and copolymerization constants values of the radical copolymerization reactions of styrene with isoprene

Comonomer		*Q-e parameters*			
M_1	M_2	e_1	Q_1	e_2	Q_2
St	Isoprene	-0.8	1	-1.21	3.32

The molecular-weight parameters of some samples of the synthesized copolymer have been studied by a method of gel-permeating chromatography and the molecular weights of the polymer have been determined.

The determined indices of the molecular weight of the copolymer obtained by this method have the following values:

Poly(styrene + isoprene): $\overline{M}_w = 724500$, $\overline{M}_n = 255500$, $\overline{M}_w/\overline{M}_n$ =2.8.

The internal macromolecule with the double bonds, incoming into composition of the styrene and isoprene copolymer, is the main factor influencing on the improvement of photosensitive properties and other lithographic properties of the copolymer [15-17].

Since the styrene and isoprene copolymer is sensitive to light and electron flow, it can be used in microelectronics as a material of negative or positive resist. At the same time, the linear structure of the macromolecule of the obtained copolymer, the availability of an internal double bond in the side fragment increase the physical-mechanical properties of this copolymer and interest for their use as an object in photochemical investigations. This polymer is sensitive to UV rays, which allows it to be used in creation of the light-sensitive material. Such cross-linked polymer has a complex of high physical-mechanical properties and meets the requirements of consumers.

It has been established that with an increase in the quantity of styrene in the composition of the copolymer, its heat-physical properties are noticeably increased. On the other hand, with the increase of quantity of fragment corresponding to isoprene monomers in the macromolecule, the elasticity property of the synthesized copolymer is increased.

It has been established as a result of the carried out investigations that the samples of the polymer coatings made on the basis of the synthesized copolymer deformed under compression without formation of cracking, which indicates that these polymers also have elastic properties. This indicates that this synthesized polymer has high brittleness, adhesion and other properties practically absent in polystyrene. The adhesion value for the styrene copolymer with isoprene is 10 MPa. It should also be noted that the improvement of the properties of this copolymer occurs due to the double bonds contained in the macromolecule [18,19].

The areas of the practical use of the synthesized copolymer have been determined. The copolymer is very easily subjected to UV radiation and forms a resist of negative type. It has been detected that the synthesized polymer is easily structured by UV rays and forms a resistive material of negative type. The photosensitivity of the styrene copolymer with isoprene is Ψ=53 cm^2/Cl. It was found that at the first moment, the structuring process occurs very quickly and then lowly. The mechanism of the structuring process has been elucidated by a method of IR spectral analysis.

It has been established using the IR spectrum that the double bonds in the side chain of the macromolecule participate in the structuring process under the action of UV rays. Both photosensitivity and physical-mechanical and heat-physical properties of copolymers strongly depend on the molar ratio of monomer residues in the copolymer. It should be noted that besides photosensitivity, the copolymer has very good adhesive, covering and other lithographic properties. At the same time, one can direct some physical-mechanical and heat-physical properties of this synthesized copolymer in the right direction.

III. CONCLUSIONS

1. The radical copolymerization reactions of α-methylstyrene with isoprene have been carried out. It has been established that the relative activity of α-methylstyrene is higher than the relative activity of the isoprenine monomer ($r_1 > r_2$), $r_1 = 2.1$; $r_2 = 0.28$.
2. The photosensitivity of the copolymer has been established (Ψ=53 cm^2/Cl). The initial stage of structuring occurs very quickly, then slowly. The copolymer adhesion index is 10 MPa.
3. The indices of the molecular-weight of the copolymer have been determined: Poly(styrene + isoprene): $\overline{M}_w$ =724500, $\overline{M}_n$ =255500. $\overline{M}_w / \overline{M}_n$ =2.8.

REFERENCES

[1]. Bulgakova, S.A., Mazanova, L.M., Lopatin, L.Ya. et al. Resists with chemical reinforcement based on the homopolymer tert butoxycarbonyloxy-styrene and its copolymer with methyl methacrylate. High-molecular compounds. 46A, 1052–1060 (**2004**).

[2]. Kim, J.M., Sneha, B. Chakrapani and Bryan S. Beckingham. Tuning Compositional Drift in the Anionic Copolymerization of Styrene and Isoprene. Macromolecules. 53, 3814–3821 (**2020**). https://doi.org/10.1021/acs.macromol.0c00526

[3]. Nakahara, A., Satoh, K., Saito, H., Kamigaito, M. Intramolecular friedel-crafts cyclization and subsequent hydrogenation of styrene-isoprene random copolymers prepared by anionic polymerization for thermally-resistant and optical applications. Journal of Polymer Science Part A, Polymer Chemistry. 50, 1298–1307 (**2011**). https://onlinelibrary.wiley.com/doi/abs/10.1002/pola.25894

[4]. Klinpituksa, P., Chaisuriyathepkul, A., Phinyocheep, P., Nakason, C., Kittipoom, S. Synthesis of acrylated styrene-isoprene-styrene copolymer. e-Polymers. 8, 1627–1635 (**2008**). https://doi.org/10.1515/epoly.2008.8.1.1627

[5]. Nakahara, A., Satoh, K. and Kamigaito, M. Cycloolefin Copolymer Analogues from Styrene and Isoprene: Cationic Cyclization of the Random Copolymers Prepared by Living Anionic Polymerization. Macromolecules. 42, 620–625 (**2009**). https://pubs.acs.org/doi/abs/10.1021/ma802024t

[6]. Li Aixiang, Lu Zaijun. Synthesis and properties of comb-like branched copolymers. Acta polum. Sin. 3, 203–208 (**2008**).

[7]. Auzez, A., Yasemin, K. Viscometric study on the miscibility of polysterene/brominated polystyrene. Eur. Polum. J. 43, 410–415 (**2007**).

[8]. Song, Rui, Jang, De-bin, Hi, Ling–hao, Yao, Guang-tao. Miscibility and morpholojy of thin films of blends of polysterene with brominated polystyrenes: effects of varying the molecular weight, bromination degree and annealing. Chin J. Polum. Sci. 24, 515–528 (**2006**).

[9]. Alexandrova, E.P., Gorikhman, M.Ya., Subbotina, L.I. et al. Optical and lightsensitive properties of comb-like polyamidoimides. Physics and Technology of semiconductors. 37, 849–852 (**2003**).

[10]. Steube, M., Johann, T., Galanos, E., Appold, M., Rüttiger, C., Mezger, M., Gallei, M., Axel, H., Müller, E., Floudas, G. and Frey, H. Isoprene/Styrene Tapered Multiblock Copolymers with up to Ten Blocks: Synthesis, Phase Behavior, Order, and Mechanical Properties. Macromolecules. 51, 10246–10258 (**2018**). https://pubs.acs.org/doi/abs/10.1021/acs.macromol.8b01961

[11]. Steube, M, Johann, T., Hübner, H., Koch, M., Dinh, T., Gallei, M., Floudas, G., Frey, H., Axel, H. and Müller, E. Tetrahydrofuran: More than a "Randomizer" in the Living Anionic Copolymerization of Styrene and Isoprene: Kinetics, Microstructures, Morphologies, and Mechanical Properties. Macromolecules. 53, 5512–5527 (**2020**). https://pubs.acs.org/doi/abs/10.1021/acs.macromol.0c01022

[12]. Stadermann, J., Riedel, M., Voit, B. Multifunctional Block Copolymers Based on Styrene Derivatives. Macromolecular Chemistry and Physics. 214, 263–271 (**2013**). https://doi.org/10.1002/macp.201200409

[13]. Valente, A., Zinck, P., Mortreux, A., Visseaux, M. Borohydrido rare earth based coordinative chain transfer copolymerization: A convenient tool for tuning the microstructure of isoprene/styrene copolymers. Journal of Polymer Science Part A, Polymer Chemistry. 49, 1615–1620 (**2011**). https://onlinelibrary.wiley.com/doi/abs/10.1002/pola.24585

[14]. Nagata, Y., Masuda, J., Noro, A., Cho, D., Takano, A., Matsushita, Y. Preparation and characterization of a styrene−isoprene undecablock copolymer and its hierarchical microdomain structure in bulk. Macromolecules. 38, 10220–10225 (**2005**). https://doi.org/10.1021/ma051681r

[15]. Gonon, L., Gardette, J.-L. Photooxidation mechanism of styrene–isoprene copolymer: evolution of the profile of oxidation according to the composition. Polymer. 41, 1669–1678 (**2000**). https://doi.org/10.1016/j.eurpolymj.2009.04.025

[16]. Park, M.J., Char, K., Park, J., and Hyeon, T. Effect of the Casting Solvent on the Morphology of Poly(styrene-b-isoprene) Diblock Copolymer/Magnetic Nanoparticle Mixtures. Langmuir. 22, 1375–1378 (**2006**). https://doi.org/10.1021/la052218a

[17]. Jenczyk, J., Makrocka-Rydzyk, M., Wypych, A., Głowinkowski, S., Jurga, S., Radosz, M. The phase structure and molecular dynamics in poly(styrene-b-isoprene) diblock copolymer. Journal of Non-Crystalline Solids. 356, 582–588 (2010). https://doi.org/10.1021/la052218a

[18]. Kim, J.M., Sneha, B. Chakrapani and Bryan S. Beckingham. Tuning Compositional Drift in the Anionic Copolymerization of Styrene and Isoprene. Macromolecules. 53, 3814–3821 (**2020**). https://doi.org/10.1021/acs.macromol.0c00526

[19]. Jong-Eun Kim, Wang-Cheol Zin, Jong-Hyun Ahn. Interfacial change on morphological transitions in styrene–isoprene diblock copolymer. European Polymer Journal. 45, 2450–2454 (**2009**). https://doi.org/10.1016/j.eurpolymj.2009.04.025