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SYNTHESIS OF AN OPTICALLY TRANSPARENT COPOLYMER ON THE BASIS OF N-VINYL CARBAZOLE AND STYRENE

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Abstract: *As a result of copolymerization of N-vinyl carbazole with styrene, the optically transparent copolymer was synthesized and the regularities of the copolymerization process, the composition and structure of the copolymer determined. The copolymerization constant values were determined by the Fineman–Ross method (r_1=0.032, r_2=5.5). It found that the styrene shows higher activity than N-vinyl carbazole. The parameters value of the copolymer microstructure was reveled. The obtained copolymer has a sufficiently high light-refractive index (n_D^{20}=1.6504). The light transmission capacity of the copolymer is 87-89%. Varying the initial composition of the copolymer, the influence of the composition on the physical-mechanical properties of the copolymer was determined. It found that with an increase in N-vinyl carbazole links, the thermal stability in the copolymer increased proportionally. It was established that the mass loss of this copolymer at 280°C during thermal degradation was ~5-6 %.*

Keywords: *N-vinyl carbazole, styrene, copolymerization, microstructure, optically transparent materials*
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Introduction

The opto- and microoptoelectronic devices of the future generation are in need of optically transparent, heat-resistant, as well as electrical-isolating materials [1-4]. This new idea for optical discoveries inspired the researchers to create new optically transparent materials. One of the perspective representatives is the copolymer of N-vinyl carbazole with styrene.

Poly-N-vinyl carbazole (PVC) is a transparent, colorless, amorphous thermoplastic polymer and has sufficiently high light transmission coefficient (n_D^{20}= 1.6830). PVC absorbs light in the UV field of the spectrum, but its photosensitivity extends to λ = 1 μm [5, 6]. The large-volume carbazole groups add this polymer a relatively high heat resistance, which is higher than polymethylmethacrylate and polystyrene (PS) ($\rho_v = 10^{13}$-10^{15} Om·m) [7, 8].
PS has a high degree of optical transparency, excellent dielectric properties [9-12]. At the same time, the specific weight of PS is low and is easily processed. However, PS is a hard fragile amorphous polymer with low mechanical strength and chemical resistance [13-14].

PS is rarely used in its pure form due to the above-mentioned weak properties. In order to increase the flexibility and heat resistance of PS and decrease its solubility, the styrene is purposefully copolymerized with other monomers. Also, the styrene is modified by monomers with sufficiently optical transparency and high physical-chemical properties [15-18]. As a result, the improved material with a unique set of properties is obtained.

The main purpose of this paper is the preparation of new heat-resistant optically transparent polymer material. For this purpose, the copolymerization of N-vinyl carbazole (VC) with styrene was carried out. The dependence of the composition of the copolymer on the composition of the mixture of monomers was investigated by changing the molar ratio of

monomers in wide range. The indices of optical transparency and light transmission of the obtained copolymer were determined.

Results and discussion

Using IR spectral analysis of the copolymer, the availability of the following absorption bands has been shown: 753 cm^{-1}, 696 cm^{-1} (CH unsubstituted phenylene rings of carbazole nucleus); 839 cm^{-1} (C-N aliphatic nitrocompound), 1598, 1492 cm^{-1} (benzene nucleus), (Fig. 1). In the IR spectrum of copolymer on the basis of VC and styrene, the valence vibrations of the vinyl bond in the field of 1630-1635 cm^{-1} are not observed.

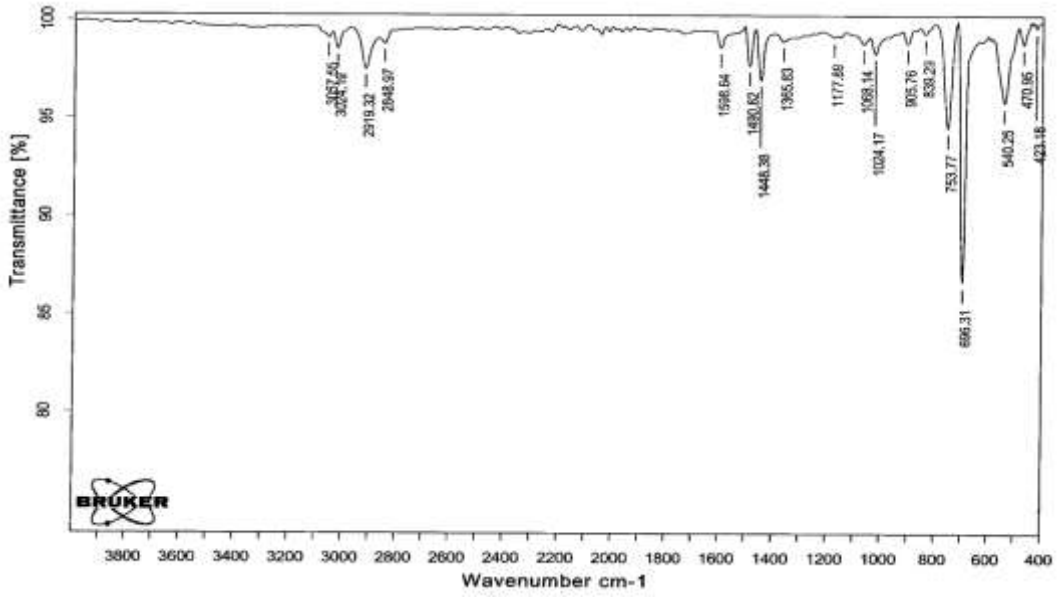
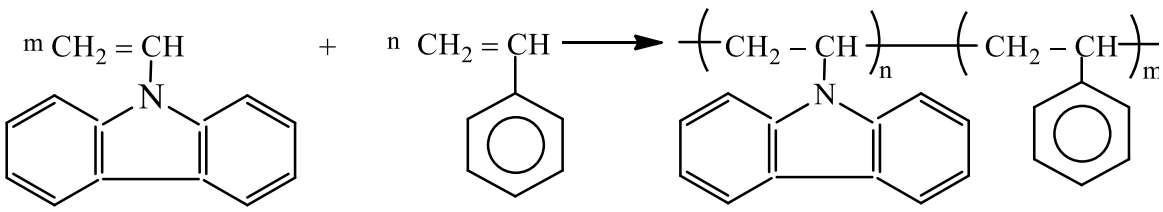


Fig. 1. IR spectrum of VC copolymer with styrene.

The link content in the copolymer was established on the nitrogen element in VC. It found that the copolymerization reaction proceeds with the opening of the vinyl group in VC and styrene monomers.

The synthesized copolymer is a white solid substance, which is soluble in benzene, chloroform and carbon tetrachloride.

The structure of VC copolymer with styrene can be presented as follows:



The copolymerization constants of monomers of VC (M_1) and styrene (M_2) were established by the Fineman-Ross method (Fig. 2), and the activity coefficients were calculated according to the Alfrey-Price's Q-e scheme (Table 1). The found copolymerization constants values r_1 and r_2 ($r_1<r_2$) found that M_1 monomer shows less activity than M_2 monomer in the radical copolymerization, and this difference was due to the chemical nature and activity of molecules in M_1 and M_2 monomers.

The increase of the quantity of VC in the

initial mixture in the range of 10÷90 mol. % leads to the increase of mols% of links of carbazole-type in the composition of copolymers up to ~1.95-44.42 mol.%. At this time, the quantity of N atoms in the composition of copolymers is naturally increased from 0.3% to 13.65%, and in parallel the quantity of styrene links is decreased from 98.05% to 55.58%.

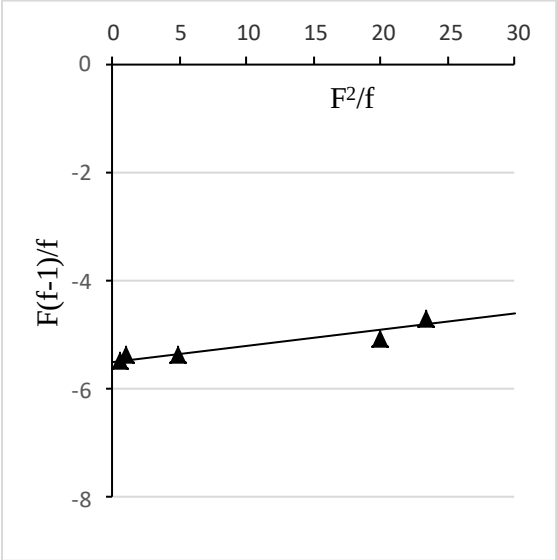


Fig. 2. The dependence of F/f(f-1) on F_2/f for determination of the copolymerization constants r_1 and r_2 by the Fineman and Ross method.

Table 1. Conditions of the copolymerization reaction and the quantity of various links (t=70ºC, Initiator – BP)

Quantity of monomers in the initial mixture, mol %		Conversion, %	Quantity of monomers in the polymer chain, mol %		Copolymer	r_1	r_2
M_1	M_2		m_1	m_2	N, %		
10	90	11 30 69	1.95	98.05	0.3	0.032	5.5
25	75	12 32 74	12.85	87.14	2.62		
50	50	14 36 81	16.88	83.12	4.72		
75	25	20 43 85	27.85	72.15	10.01		
90	10	35 56 92	44.42	55.58	13.65		

Q_1=0.41, e_1=1.40; Q_2=1.00, e_2=-0.80

In all cases of comonomers conversion, the polymer is soluble. Consequently, in the copolymerization process, the chain transfer to the polymer or structuring processes does not practically occur.

The parameters of the copolymer microstructure were established. It can be seen from values of the microstructure parameters that the minimal blocking of m_2 links is observed in the quantities of ~27.85÷72.15 mol% and ~44.42÷55.58 mol%. The high values of the Harwood constant are consistent namely with this interval of capacities in m_2 (Table 2).

Table 2. Microstructure parameters of copolymers of VC+St obtained at various initial molar ratios of monomers

№	Composition of initial mixture mol.%		Composition of copolymers, mol.%		Copolymer microstructure		
	M_1	M_2	m_1	m_2	LM_1	LM_2	R
1	10	90	1.95	98.05	1.003	50.5	3.88
2	25	75	12.85	87.14	1.01	17.5	10.80
3	50	50	16.88	83.12	1.032	6.5	26.55
4	75	25	27.85	72.15	1.096	2.83	50.94
5	90	10	44.42	55.58	1.28	1.61	69.01

L_{M_1} and L_{M_2} – average length of monomer link blocks; R – Harwood's block factor

Changing the ratio of styrene and VC in the initial mixture of monomers, one can vary the composition of the macromolecule and, apparently, the average molecular weight values of the copolymer, and as a result, the glass transitions temperature and the degree of swelling of the copolymer in solvents. As the content of m_1 fragment in the copolymer increases, the thermal stability of the polymer increases. The increase of a quantity of link of styrene type in the composition of copolymers leads to an increase of the optical transparency values of the copolymers.

The optical transparency of the obtained copolymer was determined on the device Anton Paar Abbemat 200. The given index is equal to n_D^{20} = 1.6504. Also, it was established that the light transmission of the copolymer is 87-89%.

The study of the heat-physical properties of a material made from VC copolymer with styrene is an important condition for determination of the areas of its further application. The heat resistance of this copolymer depends to some extent on its composition. Thus, with an increase of the content of links in the composition of copolymer, the thermal stability of the copolymer increases proportionally. It found that the mass loss of this polymer at 280°C during thermal destruction is ~ 5-6%. The products made from styrene copolymers (about 15%) and vinyl carbazole are notable for high heat resistance. The beginning of deformation of such products under load is observed only at 127°C (instead of 70-75°C for polystyrene products). The advantage of this copolymer over other styrene copolymers is that it maintains the good dielectric properties inherent to PS and PVC.

The obtained polymer has a sufficiently high optical transparency and heat resistance. The obtained polymer can be used in the manufacture of appropriate details of optics, micro- and optoelectronics.

Experimental part

The reaction of radical binary copolymerization was carried out at various molar ratio of VC and styrene, in ampoules, in the presence of the initiator of benzoyl peroxide, in a thermostat, at temperature 70°C for 3-4 h.

The copolymer was precipitated with methanol, washed and dissolved in benzene and purified by re-precipitation in methanol. The

isolated polymer was first dried at room temperature, and then in a vacuum box at 313 K and its weight was established.

The characteristic viscosity of the polymer was specified in Ostwald viscometer in a benzene solution at 20°C ([η]=1.16 dl/g for copolymer of VC + styrene). The viscosity was established for the copolymer of VC + styrene including 23.44 and 41.66 mol% VC links, respectively.

The results of elemental analysis are as follows (%): C-88.88; H-6.39, N-4.7, found (%): C-88.25; H-5.92, N-4.5.

The composition of the copolymer was calculated on the content of nitrogen groups established on the methodology given in [19].

When establishing the copolymerization constant, the conversion of monomers was 8-10%. However, during the synthesis and investigation of the copolymers, the conversion was 80%.

The deformation of the copolymer under the influence of heat under load was studied on the device "Kanafts". The parameters of the copolymer microstructure were established using the equation from the work [20].

IR spectra of the initial monomers and the synthesized copolymer were registered on the spectrometer "Agilent Cary 630 FTIR" of the firm "Agilent Technogies".

The refractive index was determined using a device Anton Paar Abbemat 200.

The spectral transmission coefficients of the copolymer samples were measured using SF-46 spectrophotometer in the wavelength range – 200-1000.

Conclusions

The copolymerization constant values of copolymers (r1=0.032, r2=5.5) have been found. It has been established that M_2 monomer shows higher activity than M_1 monomer in the radical copolymerization.

The optical transparency of the synthesized copolymer is n_D^{20} = 1.6504, light transmission – 87-89%.

It found that the copolymer of VC with styrene has good dielectric properties characteristic for PS and PVC. The loss of its mass at 280°C during thermal destruction is ~ 5-6%.

References

1. Morales-Masis M., De Wolf S., Woods-Robinson R., Ager J. W., Ballif C. Transparent Electrodes for Efficient Optoelectronics. *Advanced Electronic Materials.* 2017, vol. 3, no. 5, 1600529. https://doi.org/10.1002/aelm.201600529
2. Chandrinos A. Review of Polymers and Plastic High Index Optical Materials. *Journal of Materials Science Research and Reviews.* 2021, vol. 7, no. 4, pp. 1-14.
3. Scharfe B., Lehmann S., Gerdes T., Brüggemann D. Optical and Mechanical Properties of Highly Transparent Glass-Flake Composites. *Journal of Composites Science*. 2019, no. 3, p. 101. DOI:10.3390/jcs3040101.
4. Ritchie A.W., Cox H.J., Gonabadi H.I., Bull S.J., Badyal J.P.S. Tunable High Refractive Index Polymer Hybrid and Polymer− Inorganic Nanocomposite Coatings. *ACS Applied Materials & Interfaces*. 2021, vol.13, no. 28, pp. 33477−33484. DOI: 10.1021/acsami.1c07372
5. Wei Q., Pötzsch R., Liu X., Komber H., Kiriy A. and ets. Hyperbranched Polymers with High Transparency and Inherent High Refractive Index for Application in Organic Light-Emitting Diodes. *Advanced Functional Materials.* 2016, vol. 26, no. 15, DOI:10.1002/adfm.201504914
6. Tameev A.R., Lypenko D.A., Vannikov A.V., Nikitenko V.R. Transition electroluminescence and anomalous dispersion of charge carriers in thin polymer films. *Physics of the solid state.* 2009, vol. 51, pp. 1954-1960.

https://doi.org/10.1134/S1063783409090315
7. Andy Ying-Guey Fuh, Ko Nan Chen, Shing-Trong Wu. Smart electro-optical iris diaphragm based on liquid crystal film coating with photoconductive polymer of poly(N-vinylcarbazole). *Applied Optics***.** 2016, vol. 55, no. 22, pp. 6034-6039. https://doi.org/10.1364/AO.55.006034
8. Ghosh D., Sardar P.S., Biswas M., Mondal A., Mukherjee N. Dielectric characteristics of poly(N-vinylcarbazole) and its nanocomposites with ZnO and acetylene black *Materials Chemistry and Physics.* 2010, vol. 123, pp. 9-12. https://doi.org/10.1016/j.matchemphys.2010.04.019
9. Wünsch J.R. Polystyrene ― synthesis, production and applications. UK: Rapra Technology Ltd. 2000, 176 p.
10. Zhou R-J., Burkhart T. Optical properties of particle-filled polycarbonate, polystyrene, and poly(methyl methacrylate) composites. *Journal of Applied Polymer Science*. 2010, vol. 115, pp. 1866-1872. https://doi.org/10.1002/app.31331
11. Mahasin F. Hadi Al-Kadhemy & Zahraa Sabaah Rasheed. Effect of Doping Ratio on Optical Properties of Coumarin Doped Polystyrene films. *International Journal of Application or Innovation in Engineering & Management*. 2013, vol. 2, no 8, pp. 2319 – 4847
12. Satterthwaite K. Plastics Based on Styrene. Plastics Materials: Eighth Edition Elsevier Ltd. 2016: 311-328.
13. Castro GB, Carmona LO, Florez JO. Production and characterization of the mechanical and thermal properties of expanded polystyrene with recycled material. Ing. Univ. Bogota, Colombia. 2017; 21 (2): 177-194. doi:org/10.11144/Javeriana.iyu21-2.mtpe
14. Guy Clarence Semassou, Tognon Clotilde Guidi, Chakirou Akanho Toukourou, V. Z. Murielle Assogba Wounon, Antoine Vianou, Gérard Degan. Characteristics of cooked bricks with incorporation of expanded polystyrene used in building construction *Vestnik of the Astrakhan State Technical University*. 2017, no. 2, pp. 51-60. https://doi.org/10.24143/1812-9498-2017-2-51-60
15. Worzakowska M. Thermal and mechanical properties of polystyrene modified with esters derivatives of 3-phenylprop-2-en-1-ol. *Journal of Thermal Analysis and Calorimetry*. 2015, vol. 121, pp. 235–243. https://doi.org/10.1007/s10973-015-4547-7
16. Melnikov A.B., Polushina G.E., Antonov E.A., Ryumtsev E.I., Lezov A.V. Hydrodynamic and electrooptical properties of dendron modified polystyrene molecules in toluene // Polymer Science, Series A. 2000, vol. 42, pp. 760-764.
17. Castro G.B., Carmona L.O., Florez J.O. Production and characterization of the mechanical and thermal properties of expanded polystyrene with recycled material *Ingenieria y Universidad*. 2017, vol. 21, pp. 177–194. https://doi.org/10.11144/Javeriana.iyu21-2.pcmt
18. Fozilov S.F., Mavlonov B.A., Khudoynazarova G.A., Sanoyev A.C. Study of the radical copolymerization of heterocyclic industrial acrylic acids with styrene. *Young scientist.* 2015, no. 11, pp. 499-501. (In Russian).
19. Braun D., Çerdron H., Rehan M., Ritter H., Voyt B. Polymer synthesis: Theory and practice fundamentals, methods, experiences. Springer /Sci-Tech/Trade. 2014, 404p.
20. Zilberman E.N. The parameters of microstructure of multicomponent copolymers *Polymer Science. Series B.* 1979, vol. 21, no. 1, pp. 33-36. (in Russian).

N-VİNİLKARBAZOL VƏ STİROL ƏSASINDA OPTİKİ ŞƏFFAF BİRGƏPOLİMERİN SİNTEZİ

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Xülasə: N-vinilkarbazolun stirol ilə birgəpolimerləşməsi həyata keçirilməsi nəticəsində optiki şəffaf birgəpolimer sintez edilmişdir. Birgəpolimerləşmə prosesinin qanunauyğunluqları, birgəpolimerin tərkib və quruluşu müəyyən edilmişdir. Fayneman-Ross üsulu ilə birgəpolimerləşmə sabitlərinin qiymətləri müəyyən edilmişdir (r_1=0.032, r_2=5.5). Aşkar edilmişdir ki, stirol N-vinilkarbazola nisbətən daha yüksək aktivlik göstərir. Birgəpolimerin mikroquruluş parametrlərinin qiyməti müəyyən edilmişdir. Əldə olunan birgəpolimer kifayət qədər yüksək işıqsındırma göstəricisinə (n_D^{20} = 1.6504) malikdir. Birgəpolimerin işıqburaxma qabiliyyəti 87-89% təşkil edir. İlkin monomer tərkibini müxtəlif nisbətdə dəyişməklə alınan birgəpolimerin tərkibinin onun fiziki-mexaniki xassələrinə təsiri müəyyən edilmişdir. Belə ki, birgəpolimerin tərkibində N-vinilkarbazolun manqalarının miqdarı artdıqca birgəpolimerin temperaturaya davamlılığı düz mütənasib olaraq artır. Müəyyən edilmişdir ki, termodestruksiya zamanı bu birgəpolimerdə 280°C-də kütlə itgisi ~5-6%-ə bərabərdir.
Açar sözlər: N-vinilkarbazol, stirol, birgəpolimerləşmə, optiki şəffaf birgəpolimer.

СИНТЕЗ ОПТИЧЕСКИ ПРОЗРАЧНОГО СОПОЛИМЕРА НА ОСНОВЕ N-ВИНИЛКАРБАЗОЛА И СТИРОЛА

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Аннотация: В результате сополимеризации N-винилкарбазола со стиролом синтезирован оптически прозрачный сополимер. Определены закономерности процесса сополимеризации, состав и структура сополимера. Значения констант сополимеризации определяли методом Фейнемана – Росса (r_1=0.032, r_2=5.5) Установлено, что стирол проявляет более высокую активность, чем N-винилкарбазол. Определено значение параметров микроструктуры сополимера. Полученный сополимер имеет достаточно высокий показатель светопреломления (n_D^{20}=1.6504). Способность светопропускания сополимера составляет 87-89%. Варьируя исходный состав сополимера определено влияние состава на физико-механические свойства сополимера. Выявлено, что с увеличением N-винилкарбазолных звеньев пропорционально возрастает термостойкость сополимера. Установлено, что потеря массы этого сополимера при термодеструкции при 280°C составляет ~5-6 %.
Ключевые слова: N-винилкарбазол, стирол, сополимеризация, микроструктура, оптически прозрачные материалы