



УДК 535.3+541.64

Optical properties of hypercrosslinked polystyrene sorbents

Tsyurupa M.P.¹, Klimova T.P.¹, Blinnikova Z.K.¹, Davidovich Yu.A.¹,
Davankov V.A.¹, Baranov A.N.², Anan'eva M.P.²

¹*Nesmeyanov Institute of Organo-Element Compounds, Russian Academy of Sciences, Moscow*

²*Lomonosov Moscow state university, Moscow*

Поступила в редакцию 29.01.2016

Optical properties of hypercrosslinked polystyrene with the degree of crosslinking of 60 to 500% were studied by using both the absorption spectra and diffusive reflection spectra in the range of 240-850 nm. Two unusual effects were found out. The first effect consists of a dramatic band broadening and shifting its maximum with the increasing crosslinking density. It is engendered by the change in the electron structure of aromatic chromophores. The second phenomenon represents an unusual dependence of the band form and its position on the size of particles: small particles of 50 μm and less in size generate relatively narrow bands which maximum locates largely in the UV range, while large beads of 300 to 500 μm in diameter absorb the light nearly in the entire visible range. Fluorescence spectra also differ for small and large particles.

Keywords: hypercrosslinked polystyrene, absorption spectra, fluorescence spectra

Оптические свойства сверхсшитых полистирольных сорбентов

Цюрупа М.П.¹, Климова Т.П.¹, Блинникова З.К.¹, Давидович Ю.А.¹,
Даванков В.А.¹, Баранов А.Н.², Ананьева М.П.²

¹*ФГБУН Институт элементоорганических соединений им. А.Н. Несмеянова РАН, Москва*

²*Московский государственный университет им. М.В. Ломоносова, Москва*

Оптические свойства сверхсшитого полистирола со степенями сшивания от 60 до 500% были изучены с помощью спектров поглощения и спектров диффузного отражения в области длин волн 240-850 нм. Были обнаружены два необычных эффекта. Первый эффект заключается в резком уширении полосы поглощения и сдвиге её максимума с увеличением степени сшивания полимеров, что вызвано изменением электронной структуры ароматических хромофоров. Второе явление представляет собой необычную зависимость формы полосы поглощения и её положения от размера частиц: маленькие частицы размером 50 мкм и меньше дают относительно узкие полосы, максимум которых лежит главным образом в УФ области, тогда как целые большие гранулы диаметром 300-500 мкм поглощают свет практически во всей видимой области. Спектры флюоресценции также отличаются для больших и маленьких частиц.

Ключевые слова: сверхсшитый полистирол, спектры поглощения, спектры диффузного отражения, спектры флюоресценции.

Introduction

Nowadays hypercrosslinked polystyrene (HP) represents an acknowledged leader of all the polymeric adsorbing materials. HP owes its excellent reversible adsorption

capacity to the unique structure and unusual properties which result from the very principle of preparation of hypercrosslinked networks. Hypercrosslinked polystyrene has usually been obtained by an intensive crosslinking of strongly solvated polystyrene chains with numerous rigid bridges-struts [1]. This approach leads to the formation of rigid openwork-type single-phase (homogeneous) networks. Various organic bi-functional compounds were suggested to be used as crosslinking agents, however, monochlorodimethyl ether (MCDE) proved to be the most popular because of its high reactivity. The reaction of the ether with polystyrene proceeds in the presence of Lewis acids through the intermediate stage of substituting phenyl rings with chloromethyl groups. Then, the latter alkylate phenyls of neighboring polystyrene chains thus combining them with methylene links [2]. Since the conversion of MCDE in the reaction has always been complete, we used to calculate the network crosslinking degree as the molar portion of diphenylmethane-type bridges in the total number of network structural elements, i.e. bridges and unsubstituted phenyl rings. For instance, when one mole of styrene repeating units reacts with 0.3 mole MCDE, each six of ten phenyl rings are connected to each other by methylene groups, thus forming three diphenylmethane-type bridges, and the degree of crosslinking (expressed in percent) amounts to 43%. Similarly, bridging of polystyrene with 0.5 mole MCDE results in obtaining of a network in which each two phenyl rings are combined with $-CH_2-$ groups and so its crosslinking degree is 100%.

We have recently demonstrated, however, that the extent of phenyl rings mutual connectivity can be attained that is much higher than the above outlined one methylene group per two phenyl rings [3]. For that reason, now we give another, more meaningful and more general definition of the degree of network crosslinking. We relate it to the number of methylene groups binding any phenyl ring to its adjacent phenyls. We attribute the crosslinking degree of 60 (HP-60), 100 (HP-100), 200 (HP-200), 300 (HP-300), 400 (HP-400) and 500% (HP-500) to the networks prepared by bridging polystyrene with 0.3, 0.5, 1.0, 1.5, 2.0 and 2.5 mole MCDE, respectively. In the resulting networks 0.6, 1, 2, 3, 4 and 5 methylene groups bind each phenyl ring to its neighbors. Moreover, the new definition covers networks crosslinked with other by- and poly-functional reagents such as p-xylylene dichloride or tris-chloromethylmesitylene. In such cases, cross-bridges formed are different from the above mentioned diphenylmethane-type bridges.

Regardless of crosslinking density, two basic physical properties distinguish hypercrosslinked polystyrene from any other densely crosslinked polymeric network. First, the dried hypercrosslinked polystyrene swells (increases in volume) in all liquids and gases, irrespective of their thermodynamic affinity to the polystyrene-precursor. This amazing expansion of the hypercrosslinked polystyrene arises from the relaxation of strong inner stresses on contacting the dry unsolvated hypercrosslinked network with liquids or gases [4].

Second, the apparent inner surface area of the single-phase hypercrosslinked material amounts to 1000-2000 m^2/g . The huge free volume in the network, being simply a space between struts-separated polystyrene chains, is formed by increments of 1.5-3 nm in size which, as a matter of fact, are considered to be "pores" in the porous hypercrosslinked material. These pores have no real solid walls. We deal here with a new type of porosity.

As it turned out, a simple increase in the network degree of crosslinking till the ultimately possible values of 300, 400 and 500% results in emerging of new, no less surprising properties, apart from the above-mentioned ones. Indeed, as opposed to the starting polystyrene, HP-500 produces a strong electron spin resonance signal. The material is not anymore a typical dielectric, instead, its electrical resistance is pretty close to that of semiconductors.

Moreover, the ultimately crosslinked networks containing no specially introduced functional groups, retain reversibly mineral acids, salts and bases [3]. At that, the volume of dry HP-500 sample, when swollen in concentrated hydrochloric acid, or concentrated ammonium hydroxide, or toluene, rises to the same extent - by a factor of 1.6. In addition, we paid attention to the fact that, with increasing the crosslinking degree, the color of polymeric beads becomes darker so that large beads of ultimately crosslinked networks look like black ones in reflected light. At the same time they are transparent and crimson in strong through-passing light. Being interested in this phenomenon, we studied more closely the optical properties of hypercrosslinked polystyrene, namely, the absorption and diffusive reflection spectra were reordered in UV and visible ranges. Besides, some spectra of fluorescence were analyzed. This paper discusses the results obtained.

Experiment

Hypercrosslinked polystyrene networks were prepared by crosslinking beads (largely 0.3-0.5 mm in diameter) of a styrene-0.5% divinylbenzene (DVB) copolymer, pre-swollen in 1,2-dichloroethane, with 0.3, 0.5, 1.0, 1.5, 2.0 and 2.5 mole MCDE in the presence of one mole of tin tetrachloride per mole of the ether. The particular protocol of synthesis was published elsewhere [4].

3.2 μm monosized microbeads of styrene-1% DVB copolymer were obtained by precipitation polymerization and then crosslinked till 500% in accordance with the preparation protocol for the large beads. The characteristic properties of polymers under examination are given in Table 1.

Before recording spectra, a portion of large beads of each sample was ground within 5 min till obtaining irregular particles of no larger than 50 μm in size using vibration mill Manfred von Ardenne (Germany). Then, the ground particles were suspended in polydiethylsiloxane oil (about 1:10 w/v) and the suspension was sonicated for 10 min.

Absorption and diffusive reflection spectra in the range of 240-800 nm were recorded on spectrophotometer M-340 (Hitachi, Japan) equipped with an integral sphere. A thin layer of dry spherical large beads and microbeads were homogeneously distributed between two quartz windows having a free space between them of 0.5 mm in thickness. The suspension of crushed beads in silicon oil was simply blocked up between the windows. To record diffusive reflection spectra, large whole or powdered HP-500 beads were placed in the in-house made quartz cuvette of 2.5 mm in thickness.

The spectra of fluorescence were reordered on spectrofluorimeter Solar (Belarus). The excitation slit width was varied from 2 to 15 nm depending on signal intensity. The emission slit width was 2.5 nm.

Apparent inner surface area S_{app} was measured by the thermal argon desorption technique using Tswett 211 (Russia) instrument.

The residual concentration of MCDE in the reaction mixture after accomplishing the crosslinking reaction was determined by gas-liquid chromatography method by employing Sigma 2000 (Perkin-Elmer, USA) instrument.

Results and discussion

As our previous publication have documented [4, 5], the bridging of polystyrene with monochlorodimethyl ether proceeds almost quantitatively. We drew the same conclusion when analyzing the synthesis results of polymers tested in this study. Table 1

shows that MCDE consumes completely during the stage of chloromethylation: its conversion achieves 95-100%. However, for steric reasons, not all chloromethyl groups can easily find CH positions in benzene rings of neighboring chains which would be accessible for subsequent reaction of alkylation, and so the densely crosslinked HP networks contain around 3% of residual chlorine. Yet, this amount seems to be surprisingly small. Indeed, if the synthesis of HP-500 would stop on the stage of chloromethylation, the content of chlorine would be as large as 42.6%. Consequently, the real degree of crosslinking is pretty close to the nominal ultimate values.

Table 1. Characteristics of tested hypercrosslinked polymeric sorbents

Sample	Residual chlorine %	Conversion of MCDE, %	S_{app} m^2/g
HP-60	0	100	1160
HP-100	0.5	-	1000
HP-200	0.8	95.0	1160
HP-300	2.96	98.6	1170
HP-400	3.12	94.4	1200
HP-500	3.0	94.5	1200
MS-500*	4.08	99.5	560

*MS- microspheres

Fig. 1 depicts absorption spectra in the range of 240-800 nm for both the ground beads of initial styrene-1% divinylbenzene copolymer and those of hypercrosslinked networks on its basis. As can be seen, the spectrum of the initial copolymer presents an intensive and sufficiently narrow band of phenyl chromophore, the maximum of which lies at 270 nm. With introducing 60 and 100% of additional crosslinking bridges into the copolymer, the spectra become wider while their maximum shifts towards long-wave range. In the spectra of HP-60 and HP-100, besides the maxima at 306 and 320 nm, correspondingly, there remains a shoulder, its maximum coinciding with that of the initial copolymer major band. Probably, it indicates the presence in these polymers of phenyl groups which did not participate in bridging. Further increase in crosslinking density leads to the disappearance of the shoulder, greater band broadening and shifting the band maximum as far as toward 400 nm for HP-500.

The same tendency on changing the band form and maximum position with increasing crosslinking degree is also characteristic of the spectra of dry whole spherical large beads (Fig. 2). However, there are some differences. First of all, an extremely large band broadening engages our attention. Furthermore, the band maxima shift even greater compared to that of ground beads having the same degree of crosslinking. As can be seen from Fig. 2, HP-500 absorbs the visible light nearly in the entire range of wavelengths, up to 700 nm, and only on subsequent rising wavelength the light absorption drops, for that reason whole beads of HP-500 sample are black in color in reflected light, but they remain transparent for red light. Noteworthy, the aromatic networks with crosslinking degrees of 200 to 500% absorb the visible light much stronger than the UV-light.

Generally speaking, the mechanical grinding of whole beads does not change the network chemical structure; at least, FTIR spectra of polymers ground in air, argon or paraffinic oil are identical. Therefore, the spectra of whole and ground beads also would have to be identical. Nevertheless the diffusive reflection spectra confirm the dramatic difference in light absorption between large HP-500 beads and powdered HP-500 sample (Fig. 3). As one can see, the powdered ultimately crosslinked samples absorb 85-90% light in UV-range but the light reflection significantly rises with increasing wavelength in the

visible range. Contrary to this, beaded HP-500 absorbs 95% of light within the range of 350 to 850 nm.

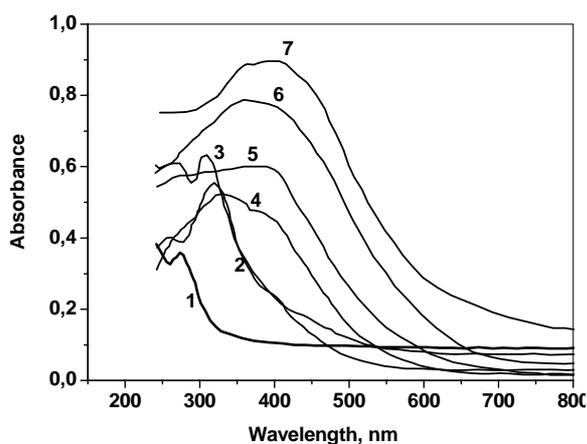


Fig. 1. Absorption spectra of ground samples recorded as suspension in silicon oil: (1) styrene-0.5% divinylbenzene copolymer, position of maximum is $\lambda_{\max}=274$ nm; (2) HP-60, $\lambda_{\max}=306$ nm; (3) HP-100, $\lambda_{\max}=320$ nm; (4) HP-200, $\lambda_{\max}=330$ nm; (5) HP-300, $\lambda_{\max}=370$ nm; (6) HP-400, $\lambda_{\max}=360$ nm; (7) HP-500, $\lambda_{\max}=398$ nm.

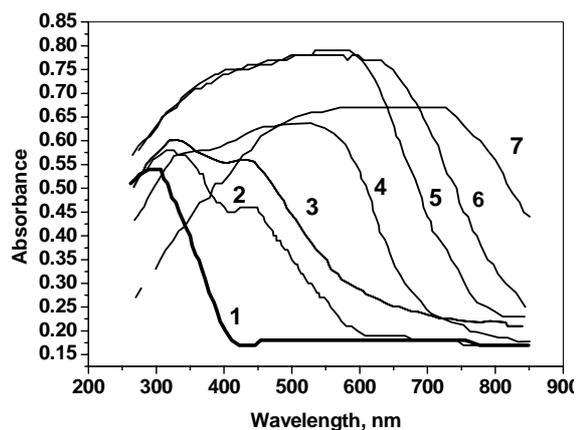


Fig. 2. Spectra of dry whole beads: (1) styrene-0.5% divinylbenzene copolymer, position of maximum is $\lambda_{\max}=300$ nm; (2) HP-60, $\lambda_{\max}=330$ nm; (3) HP-100, $\lambda_{\max}=375$ nm; (4) HP-200, $\lambda_{\max}=450$ nm; (5) HP-300, $\lambda_{\max}=590$ nm; (6) HP-400, $\lambda_{\max}=590$ nm; (7) HP-500, $\lambda_{\max}=680$ nm.

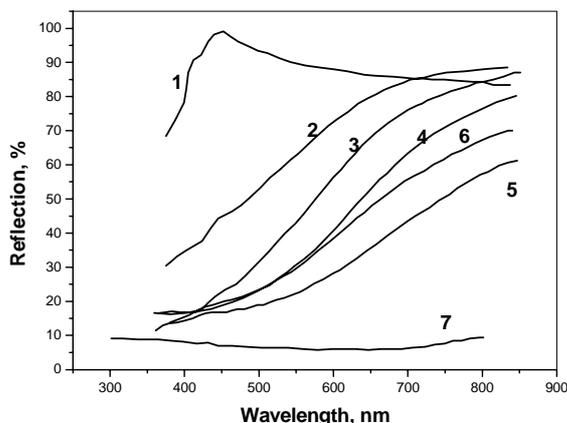


Fig. 3. Diffusive reflection spectra of ground beads measured as suspension in silicon oil: (1) initial styrene-0.5% DVB copolymer, (2) HP-100, (3) HP-200, (4) HP-300, (5) HP-400 and (6) HP-500; (7) diffusive reflection spectrum for HP-500 whole beads.

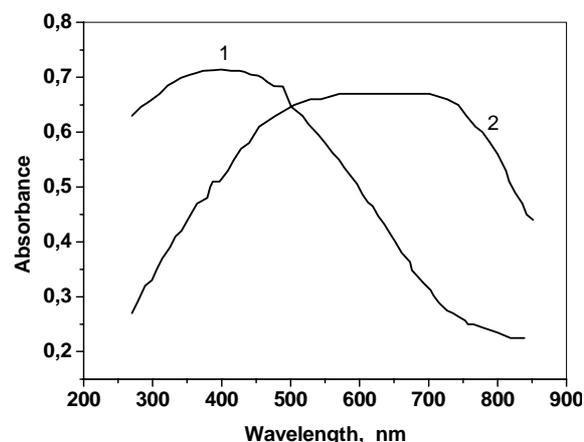


Fig. 4. Absorption spectra of whole dry beads of hypercrosslinked polystyrene with 500% crosslinking density based on (1) 0.3-0.5 mm beads of styrene-0.5% DVB copolymer and (2) monosized 3 μ m beads of styrene-1% DVB copolymer.

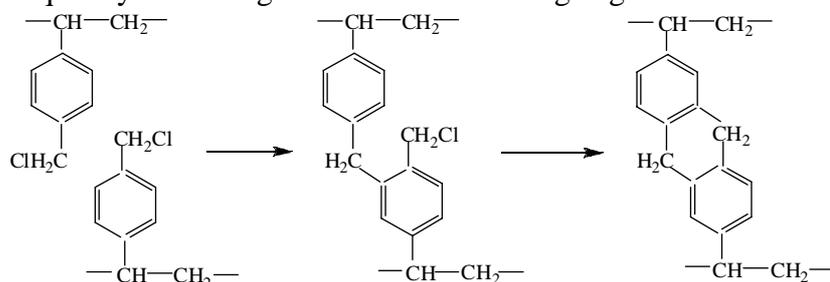
Finally, the discrepancy between large and small particles follows also from Fig. 4. The latter demonstrates the spectra of two beaded hypercrosslinked networks with a comparable crosslinking degree of about 500% prepared by bridging styrene-1% DVB monosized microbeads of 3 μ m in diameter (MS-500) and large styrene-0.5% DVB beads having diameters of 300-500 μ m (HP-500). While the large beads of HP-500 generate a wide band with flat maximum at 680 nm, the microbeads produce much narrower band

with maximum at 380 nm. We should also note that 10-50 μm irregular particles of ground HP-500 sample give narrower band than MS-500 microbeads (compare Fig. 1 and Fig. 4). Though, this discrepancy appears to be explained by the fact that the spectrum of ground HP-500 beads was recorded in silicon oil that allows minimizing the light reflection from particle outer surface and encourages the band narrowing. The maxima of the both spectra coincide.

Thus, we can state with confidence that the non-trivial fact of the dependence of the type of spectrum on particle size has reliably been established. It appears to be associated with the character of light spreading throughout the beads. However, at present we have no explicit and logic explanation of this phenomenon.

Regarding the type of the band shape and its position, in order to understand their dependence on the degree of crosslinking, first of all, we would like to consider the following circumstances. As our previous study has surely documented [4], the increasing intensity of polystyrene crosslinking with monochlorodimethyl ether via Friedel-Crafts reaction is not accompanied with appearing in final products of any new functional groups which could drastically change the type of absorption spectra. Also, the strong band broadening observed for whole beads and significant shift of band maxima with increasing crosslinking density should not result from the increase in the degree of substitution on benzene rings. Indeed, the introduction of five methyl groups into a benzene molecule, though altering its spectrum, shifts the major benzene bands to longer wave-lengths only at a short distance of about 20 nm [5]. Lastly, it is necessary to note that the formation of hypercrosslinked polystyrene network is a statistical process, it does not entail the emergence of any ordered secondary structures inclinable, for instance, to stacking interactions, which could change the spectra. So, it only remains for us to presume that the increasing crosslinking density alters the chromophore electron structure.

Indeed, the isolation of benzene chromofores is known to be incomplete after binding two benzene rings even with one methylene group [6], that is why the UV-spectrum of diphenylmethane differs noticeably from that of benzene [5]. For that reason one can perfectly assume the presence of domains with a modified electron structure already in HP-60 and HP-100, however, the fraction of such domains appears to be insufficient to tell dramatically upon the optical properties of these polymers. In the network with nominal 200% crosslinking density, Law et al. [7], by using ^{13}C magic angle spinning (MAS) NMR technique, found out a marked portion of dihydroanthracene fragments, the latter being formed by connecting two phenyl rings with two methylene bridges without adequately increasing the actual crosslinking degree of the network:



It may well be that strong inner stresses [8] emerging in dry hypercrosslinked networks (due to distortion of valence angles and bond lengths, particularly in $-\text{CH}_2-$ groups connecting phenyl rings) facilitate the dehydration of dihydroanthracene fragments and the formation of anthracene-type bridges. Obviously, with increasing crosslinking density till maximum possible values of 300, 400 and 500%, the portion of such bridges or similar aromatic hydrocarbon fragments increases, too. The formation of aromatic condensed structures entails the appearing in hypercrosslinked network of domains with

delocalized π -electrons, which imparts well-defined electron-donating properties to ultimately crosslinked networks and change their optical characteristics. In other words, the increase in number of phenyl rings participating in the delocalization of electrons, which conditions the emerging of light absorption at longer wavelengths. Therefore, the shift of band maximum with rising degree of crosslinking is deemed to be caused by the increase in the number and size of condensed aromatic hydrocarbon structures.

One can also expect that the change in polymer electron structure should tell upon the spectra of fluorescence. Fig. 5 depicts the spectrum of fluorescence for the initial styrene-DVB copolymer. Wide asymmetric luminescence bands were observed in the range of 300 to 600 nm on excitation at any wavelength ranging from 220 to 400 nm.

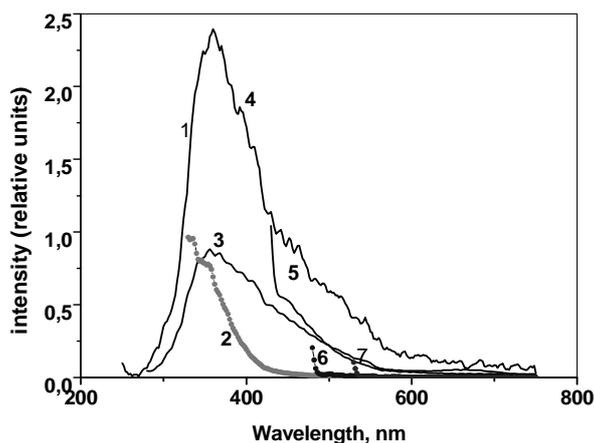


Fig. 5. Fluorescence spectra of styrene-0.5% DVB copolymer at the excitation of (1) 220 nm, (2) 250 nm, (3) 300 nm, (4) 350 nm, (5) 400 nm, (6) 450 nm, (7) 500 nm.

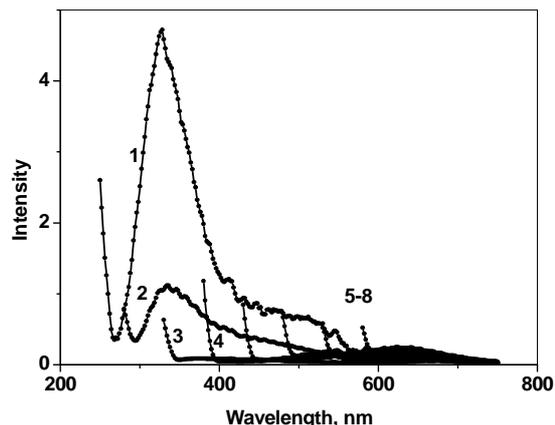


Fig. 6. The spectra of fluorescence for the ground HP-500 sample at the excitation of (1) 220 nm, (2) 250 nm, (3) 300 nm, (4) 350 nm, (5) 400 nm, (6) 450 nm, (7) 500 nm, (8) 550 nm.

The fluorescence of hypercrosslinked polystyrene networks is more intensive and manifests itself in the same range of wavelengths. Again, we see the difference in optical properties between the whole beads of HP-500 and the powdered HP-500 sample. In the spectrum of the latter a strong fluorescence emerges at 380 nm at the excitation at 220 nm (Fig. 7). With increasing wavelength of excitation the luminescence appears even at 600-700 nm.

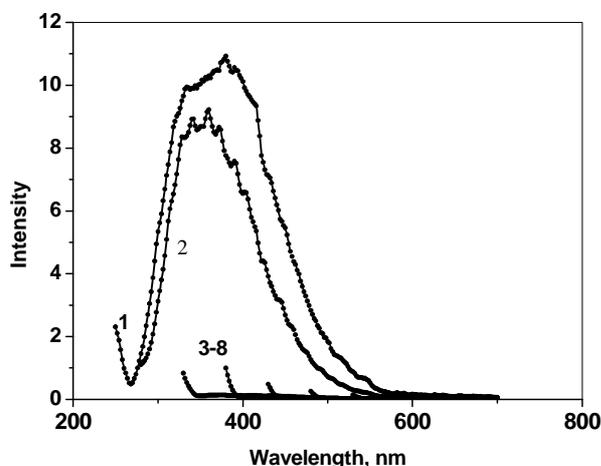


Fig. 7. The spectra of fluorescence for the beaded HP-500 sample at the excitation of (1) 220 nm, (2) 250 nm, (3) 300 nm, (4) 350 nm, (5) 400 nm, (6) 450 nm, (7) 500 nm.

The exposure of HP-500 whole beads to the light of 200 and 250 nm wavelengths results in emergence of a strong and very wide band in its spectra (Fig. 7). However, the further rise in wavelength of the exciting light does not cause the fluorescence, most probably, because of strong light absorption of the ultimately crosslinked polymer in that visible range.

Conclusion

Analysis of light absorption in the visible range by the hypercrosslinked polystyrene networks performed by means of both absorption spectra and spectra of diffusive reflection revealed two non-trivial facts. First, as the degree of crosslinking raises from 60 to 500% the absorption bands become wider and wider while their maximum shifts towards the long-wave range. At that, the light absorption in visible range becomes much stronger than that in UV-range. We hypothesize that this effects relates to the formation in highly stressed hypercrosslinked networks of condensed aromatic hydrocarbon fragments with delocalized π -electrons.

The second unusual effect consists in the influence of particle size on the band form and its position in absorption spectra, namely, 10-50 particles obtained by grinding 300-500 μm beads produce relatively narrow bands with maxima located largely in UV-range, whereas large beads give extremely wide band with "maximum" located as far as 680 nm. One can draw the same conclusion when comparing the absorption spectra of large beads and microbeads with identical crosslinking density.

The size of particles also influences the type of fluorescence spectra. The powdered polymer HP-500, being excited with the light of 220 nm wavelength, generates an intensive fluorescence till 400 nm, as well as weak fluorescence even up to 700 nm when the excitation was done at 200-600 nm. Distinctly, the irradiation of the whole beads at 220-250 nm causes an intensive fluorescence in the range of 220 to 600 nm, while further increase in the wavelength of excitation does not result in emergence of fluorescence at all. We have to avow that a real perception of this amazing phenomenon still lies ahead.

This study is supported by Russian Foundation of Basic Research, grant 15-03-01533.

References

1. Davankov V.A., Tsyurupa M.P. Hypercrosslinked Polymeric Networks and Adsorbing Materials, *Comprehensive Analytical Chemistry*, Vol. 57. Elsevier. 2011. 640 p.
2. Tsyurupa M.P., Pastukhov A.V., Blinnikova Z.K., Pavlova L.A. et al., *Polystyrene. Synthesis. Characteristics and Applications*, ed. C. Lynwood, Nova, New York, 2014, pp. 143-200.
3. Tsyurupa M.P., Blinnikova Z.K., Borisov Yu.A., Ilyin M.M. et al., *J. Separation. Sci.*, 2014, Vol. 37, No 7, pp. 803-810.
4. Tsyurupa M.P., Blinnikova Z.K., Davidovich Yu.A., Lyubimov S.E. et al., *Reactive&Functional Polymers*, 2012, Vol. 72, No 12, pp. 973-982.
5. Kusakov M.M., Shimanko N.A., Shishkina M.V. Ultraviolet absorption spectra of aromatic hydrocarbons (Russian), *Izd. Akademii Nauk SSSR, M.*, 1963, 271 p.
6. Stern E.S., Timmons C.J. Gillam and Stern's Introduction to Electronic Absorption Spectroscopy in Organic Chemistry. Edward Arnold Publishers Ltd., London, 1970, 277 p.
7. Law R.V., Sherrington D.C., Snape C.E., Ando I. et al., *Macromolecules*, 1996, Vol. 29, No 19, pp. 6284-6293.
8. Tsyurupa M.P., Papkov M.A., Davankov V.A., *Polymer Science, Ser. C*, 2009, Vol. 51, No 1, pp. 81-86.

Tsyurupa Maria P. - senior scientific fellow, doctor of chemical sciences, leading scientific fellow, Nesmeyanov-Institute of organo-element compounds RAS, Moscow, mts@ineos.ac.ru

Blinnikova Zinaida K. - senior scientific fellow, Ph.D., Nesmeyanov-Institute of organo-element compounds RAS, Moscow, 8 (499) 135 92 54, blinnikovazk@mail.ru

Davankov Vadim A. - professor, doctor of chemical sciences, head of laboratory, Nesmeyanov-Institute of organo-element compounds RAS, Moscow, 8 (499) 1356471, davank@ineos.ac.ru

Anan'eva Maria P. - student, Lomonosov-Moscow state university, Moscow, 8 (917) 528 91 63, Baranov@physics.msu.ru

Klimova Tamara P. - scientific fellow, Nesmeyanov-Institute of organo-element compounds RAS, Moscow, 8 (499) 135 92 69, tab@ineos.ac.ru

Davidovich Yurii A. - senior scientific fellow, Nesmeyanov-Institute of organo-element compounds RAS, Moscow, 8 (499) 135 65 13, yualda@rambler.ru

Baranov Avatolii N. - PhD., senior lector, Lomonosov-Moscow state university, Moscow, 8 (917) 528 91 63, Baranov@physics.msu.ru