Radiational Graft Polymerization of Hexenes on Polystyrene

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ABSTRACT

The graft polymerization of isomeric hexenes on polystyrene is carried out in order to create an electrical insulation material with improved operation characteristics. Reactions are conducted by radiational-chemical methods, applying γ-radiation and accelerated electrons.

The mechanical, thermal, structural and dielectric characteristics of modified polystyrene are investigated. The grafting is proved to be most effective with application of 4-methyl-1-pentene. Kinds and dosage of radiation are optimized.

The described method allows improvement of dielectric losses, heat resistance and thermostability of polystyrene.

Key Words: grafting, electrical insulation, characteristic improvement, accelerated electrons

INTRODUCTION

Today development of specific spheres of radioelectronics presents new requirements for the quality of applied dielectric materials. One of the reasons is the use of high frequency electric fields in radio-electronic equipment during the last few years.

In radio-electronic equipment, working in high frequency mode, heating of electric insulation materials occurs. This results in a decrease of electrical resistance in dielectric parts, which decreases their quality factor (Q). Initially, one can observe the decline of dielectric characteristics of electro-insulation materials and then their electrical breakdown. On the other hand, radio-electronic equipment often works in the presence of external thermo-mechanical exposure, which imposes additional requirements for the dielectric and physical properties.

Polystyrene ranks among the most widely applicable plastics of polymerization type. The main advantages of polystyrene (PS) are its low cost, availability of raw materials and high dielectric characteristics, which determine its use in electrotechnics, radiotechnics and electronics. However, PS has a number of disadvantages, such as low impact strength and low thermal resistance.

Various methods for increasing the impact strength of PS are known, and some of them have found application in industry. But, the use of these methods results in a considerable decrease of the dielectric properties of PS, and this is the reason why high impact PS has limited application as insulation material.

In this context, it is necessary to develop a method of production of insulation material with high operation characteristics.

To solve this problem, we have chosen the method of radiational-chemical modification of PS.
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by graft polymerization of hexenes on PS. It was supposed to combine the best properties of PS and polyhexenes, such as 4-methyl-1-pentene, 4-methyl-2-pentene, 1-hexene.

EXPERIMENTAL

Materials
The starting material of the investigation was atactic PS, synthesized by the block thermal method. Its main characteristics: density= 1.05 × 10³ kg/m³, Vicat heat resistance=356 K, strength at breakage=320 × 10⁵ N/m², breaking elongation= 2.5 %, dielectric loss tangent at 298 K and frequency of 10⁶ Hz = 5.5 × 10⁻⁴ and dielectric constant=2.78.

Series of hexene monomers were of the following purity: 4-methyl-1-pentene(4M1P), 99.9%, 4-methyl-2-pentene(4M2P), 99.7% and 1-hexene (N1H), 99.5%.

Before application, the monomers were exposed to distillation and dried over sodium wire to remove moisture.

Ionizing Radiation Sources
As the sources of γ-radiation we used two Co⁶⁰ isotope sources with activities corresponding to 21.0 and 16.2 kg-equiv.Ra. As the source of electronic radiation we used the electrons linear accelerator with 80 × 10⁻¹⁴ J full energy in maximum of energy spectrum and frequency impulses of electron flow of 400 Hz.

The intensity of radiation flow varied for γ-radiation from 0.4 to 6.0 Gy/s, and for electrons from 2.5 to 20 kGy/s.

Radiation Mode and Preparation of Polymer-Monomer System
Polymer-monomer system was prepared by keeping PS in liquid monomer at 298 K up to maximum swelling (9 × 10⁴ sec) after which, 35% monomer concentration in the swelled system is reached.

The irradiation of studied products was conducted in glass ampolles of 15 × 10⁻³ m diameter with 0.5 × 10⁻³ m side thickness. To eliminate oxygen influence on the modification process, the ampolles were deaerated after the preparation of polymer-monomer system. As it is necessary to keep the monomer concentration constant, deaerating was conducted at 77 K with preliminary blowing through the ampolles by dry nitrogen.

During irradiation, ampolles were continuously rotated for uniform distribution of radiation field. Thermostatic treatment of ampolles on irradiating by accelerated electrons was conducted by blowing round ampolles with compressed air, when the temperature of external surface of the ampolles was not more than 298–303 K. Thermostatic treatment by γ-radiation is easier, because the water layer of the source provides the necessary heat removal from the irradiated object. Water temperature also was not more than 298–303 K.

Irradiation dose intensity, both at γ-radiation and accelerated electrons radiation, varied in wide ranges by changing the distance between the source and the irradiated system. Irradiation dose was calculated as the product of irradiation time and dose intensity at a given point.

Separation of the End Product
After irradiation the polymer system was withdrawn from the reaction vessel and washed by ethyl alcohol.

As the result of washing, the monomer and its oligomers pass into alcohol solution. Then, to extend the evaporation surface of the polymer, which represents the hardened bulk, it was cut into parts of approximately 5 × 10⁻³ m size. The crushed samples were dried to constant weight for 2.16 × 10⁴ s at 373 K and at vacuum evaporation resulting in complete cleansing of the product.

Test and Investigation Methods
The complex investigation properties of the synthesized product was conducted using a number of physico-chemical analyses.

The determination of the chemical structure of the obtained products was conducted using infrared spectroscopy method. Spectra in the range
of 400–4000 cm⁻¹ were obtained by an IR-27G spectrometer.

Gel fraction was determined according to the solubility of the products in boiling solvents (benzene, cyclohexane).

The density of the obtained samples was determined by the method of hydrostatic weighing.

Differential thermal analysis was conducted using "MOM" derivatograph of PPE-type. The accuracy of thermal effects determination was 0.5 K and of gravimetric measurements, 2 × 10⁻⁷ kg. Vicat heat resistance was determined by the conventional method.

The study of mechanical characteristics (tensile strength and breaking elongation) was conducted 25 times at tensile machine RMI-250 at 298 and 353 K by the speed of 5 × 10⁻⁵ m/s.

The determination of Charpy impact strength was conducted by the standard method of pendulum type Charpy impact machine.

Dielectric constant (ε) and dielectric loss tangent (tan δ) were measured using E-9-4 Q-meter, in frequencies of 10²–10⁶ Hz and at temperatures from 298 to 473 K. Electrical strength (Eₜ) was determined using UP-1 machine in air media at 298 K. The voltage applied to the polymer increased with a constant rate of 1kV/s.

### RESULTS AND DISCUSSION

#### The Influence of the Irradiation Parameters on the Modification Process

As it is seen from Table 1, despite the similarity of the monomers chemical structure (4M1P, 4M2P, N1H), the yield of gel fraction by irradiation varies considerably with each PS-monomer system. From the obtained data (see Table 1), monomer activity can be presented as follows:

4M1P > N1H > 4M2P

So, it was found that 4M1P is the most efficient agent for PS modification (radiation curing). In this context, further investigation was conducted using 4M1P monomer.

Dose intensity is one of the main parameters determining the process kinetics. The study of copolymerization rate depending on dose intensity allows determination of the process mechanism. In this connection, we have conducted the investigation of the PS copolymerization rate dependence on the intensity of γ-radiation and the accelerated electrons radiation dose (see Table 2).

The rate of graft polymerization was determined at the point of stability, i.e., in the range of 2.0–2.5 MGy of the absorbed dose.

Authors of [1,2] showed, that with 4M1P the dependence of copolymerization rate on γ-radiation and accelerated electrons radiation dose, is represented by the following relation:

\[ V = k \cdot J^{0.54} \]

where \( V \) is the copolymerization rate, \( J \) is the dose intensity and \( k \) is the proportionality factor.

From the presented data it is seen that in the wide range of dose intensities, the exponent value is close to 0.5. This value is valid for reactions occurring according to radical mechanism with bimolecular breaking of the kinetic chain. On comparing the data presented in Table 2, one can see that the dose intensity decrease results in the increase of weight growth and gel fraction. Taking this into account, we have chosen the optimum dose for the production of modified PS, which is as follows:

γ-radiation = 2.2 Gy/s and accelerated electrons radiation = 5 kGy/s.

From Table 3 it is seen that the weight growth of the modified product is not similar in
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Table 2. The effect of radiation type and its intensity on the process of PS modification in the presence of 4M1P (irradiation dose = 2 MGy).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initiating radiation dose intensity</th>
<th>Accelerated electrons, kGy/s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>γ-Radiation, Gy/s</td>
<td>Accelerated electrons, kGy/s</td>
</tr>
<tr>
<td></td>
<td>0.55  1.10  1.65  2.20  2.75</td>
<td>2.5  5.0  10.0  15.0  20.0</td>
</tr>
<tr>
<td>Weight growth (%)</td>
<td>17.2  12.0  8.1  7.5  7.0</td>
<td>5.2  4.1  3.5  3.3  3.2</td>
</tr>
<tr>
<td>Gel fraction (%)</td>
<td>75  72  67  65  52</td>
<td>35  27  14  10  10</td>
</tr>
</tbody>
</table>

Table 3. The dependence of weight growth and gel fraction on type and dose of irradiation of the swelled polymer-monomer system.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Irradiation dose, MGy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>γ-Radiation</td>
</tr>
<tr>
<td></td>
<td>1.0  2.0  3.0  4.0  5.0</td>
</tr>
<tr>
<td>Weight growth (%)</td>
<td>4.0  7.5  10.0  12.0  15.0</td>
</tr>
<tr>
<td>Gel fraction (%)</td>
<td>35  65  78  85  85</td>
</tr>
</tbody>
</table>

the range of the studied absorption doses for both kinds of radiation. On irradiating the sample by γ-radiation and by accelerated electrons, a relatively high weight growth in the beginning of the process, up to 2 MGy dose is observed. This is supposed to be due to polymer-monomer system viscosity being insufficient at the given radiation dose for limitation of monomer mobility in swelled PS that results in free motion of monomer parts to active points of the reaction. On reaching 5–7% of weight growth, one can observe definite stability. On irradiating by γ-radiation, weight growth and gel fraction formation overlap the results by approximately 2-fold obtained on irradiating by accelerated electrons, at similar radiating doses.

Almost all chemical reactions in polymers initiated by γ-radiation and accelerated electrons radiation are specified by the effect of secondary electrons, energies of which do not differ in value order. The difference in linear transfer energy is not considerable in that case [3], and it is necessary to say that on applying these kinds of ionizing radiation, a difference in results was observed [4–6]. The most probable reason for this difference in output results (weight growth, gel fraction formation) is that the radiations differ by a few orders from each other on dose intensity, and that might be the reason for the temperature increase of the system irradiated by accelerated electrons and not observed with γ-radiation exposure.

Structure and Properties of the Modified Products

The determination of chemical structure of the synthesized products was conducted using infrared spectroscopy method. With this aim, we have obtained the spectra of the starting PS, poly(4-methyl-1-pentene) and products of radiation chemical modification of PS. Comparison of spectra of modified and standard PS (see Figure 1) showed some similarity between them. However, there are several differences in the spectra, such as those in shapes and intensities of absorption bands in 400–600 and 1300–1400 cm⁻¹ ranges. PS infrared spectrum was studied by a number of authors and a generalized interpretation of absorption bands frequencies is given [7–9].

It was shown above that irradiating of the
polymer-monomer system (PS-4M1P) results in the weight growth of the base polymer, which increases as the radiation dose increases. Analyzing the reasons for polymer weight growth, it was found that poly-4M1P spectrum, in contradiction to that of the modified product, comprises an unresolved absorption band at 1450 cm\(^{-1}\). The polymer weight growth at joint irradiating of PS and 4M1P is not the result of introduction of 4M1P homopolymer into the modified product chain because, in this case, intensive absorption at 1450 cm\(^{-1}\) must occur, but it is absent here.

On the other hand, in the spectrum of the modified product, the rise of absorption band at 1380 cm\(^{-1}\) was observed with the increase of radiation dose, i.e., with the increase of weight growth. The reason for occurrence of the absorption band at 1380 cm\(^{-1}\) in the PS spectrum is not clear, but it is hardly connected with vibration of methyl groups [8]. The rise of intensity of the band at 1380 cm\(^{-1}\) in the modified product spectrum can be related to the increase of concentration of methyl groups, because 4M1P, which was present during irradiation, has two methyl groups in its structure. To determine the structure of the said band, we conducted a differential record of the spectra of the modified product and PS in the range of 1300–1400 cm\(^{-1}\). The record showed clearly a resolved doublet, characterizing the absorption of dimethyl groups.

Absorption band at 543 cm\(^{-1}\) in the modified product spectrum is slightly widened and is less, (according to peak intensity) than the same band in the starting PS spectrum. It was shown [9], that this band is not present in the spectrum of solid crystalline PS and occurs only in its melt or in atactic PS. This fact allows us to make a conclusion that the said band characterizes the degree of

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Block PS</th>
<th>High Impact PS</th>
<th>Poly-(styrene-g-4M1P) 15%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat resistance, Vicat (K)</td>
<td>356</td>
<td>373</td>
<td>383</td>
</tr>
<tr>
<td>Thermal stability (K)</td>
<td>583</td>
<td>536</td>
<td>613</td>
</tr>
<tr>
<td>-decomposition 10%</td>
<td>593</td>
<td>553</td>
<td>638</td>
</tr>
<tr>
<td>-50%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Charpy impact resistance (kJ/m(^2))</td>
<td>19</td>
<td>57</td>
<td>43</td>
</tr>
<tr>
<td>Electrical strength (V/m)</td>
<td>(60 \times 10^6)</td>
<td>(25 \times 10^6)</td>
<td>(60 \times 10^6)</td>
</tr>
<tr>
<td>Tensile strength at 298 K (kg/m(^2))</td>
<td>(32 \times 10^5)</td>
<td>(26 \times 10^5)</td>
<td>(41 \times 10^5)</td>
</tr>
<tr>
<td>Dielectric loss tangent</td>
<td>(6 \times 10^4)</td>
<td>(4 \times 10^4)</td>
<td>(6 \times 10^4)</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>2.78</td>
<td>2.78</td>
<td>2.78</td>
</tr>
</tbody>
</table>

Table 4. Technical characteristics of styrene polymers.
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macromolecular order and occurs as the result of interaction of the aromatic ring and the main chain of the polymer. The widening of this band in the modified product spectrum is caused by changes in the main chain of the polymer or by the effect of grafted chains.

Taking into account the following facts, such as weight growth of the modified product during irradiation, absence of poly(4M1P) homopolymer in its content and intensity increase of the absorption band at 1220 and 1380 cm⁻¹, one can draw the conclusion that the studied product is a graft polymer of PS with 4M1P, namely poly(styrene-g-4M1P) of net structure.

The results of complex investigation of the modified product properties (containing 15% of grafted 4M1P) are presented in Table 4.

CONCLUSION

Graft polymerization of hexenes (4-methyl-1-pentene, 4-methyl-2-pentene, 1-hexene) on polystyrene, initiated by γ-radiation and accelerated electrons radiation, was studied. By methods of physico-chemical analysis, infrared spectroscopy, mechanics, thermography and electrophysics, the main regularities of the formation and change of properties of graft polymers of poly(styrene-g-4M1P) type were studied. It was found that the grafting process follows according to radical mechanism.

It was shown that modification of polystyrene by the suggested method allows attachment to the polymer the complex of important operational properties, such as high impact resistance, improved electrophysical properties, increased (by 27 K) heat resistance and (by 45 K) thermal stability.

The increase of 4M1P links content in poly(styrene-g-4M1P) copolymer from 1 to 15 wt.% causes the shift of dielectric loss tangent by 38 K to the side of high temperatures, preserving the starting values of dielectric loss tangent of 6 × 10⁻⁴ and dielectric constant (ε) of 2.78. Impact strength increases by 200% and tensile strength by 30%.

REFERENCES