

# Effect of Fullerenes on the Structure and Properties of Linear and Crosslinked Polyesterurethane Ureas

Y. A. Olkhov,<sup>1</sup> B. Jurkowski<sup>2</sup>

<sup>1</sup>*Institute of the Problems of Chemical Physics, Russian Academy of Sciences, 142 432 Chernogolovka, Moscow, Russia*

<sup>2</sup>*Plastic and Rubber Processing Division, Poznan University of Technology, 60-965 Poznan, Poland*

Received 5 April 2006; accepted 24 May 2006

DOI 10.1002/app.24870

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Small concentrations up to  $10^{-6}$  mol/cm<sup>3</sup> of C<sub>60</sub> fullerenes influence on both the molecular and topological structures changing at synthesis and the related mechanical properties of linear (pseudonetworked) and crosslinked polyester urethane ureas (PEUU). A crosslinked PEUU was synthesized on the base of poly(oxypropylene) macrodiisocyanate (POPMDIC) and 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) with virtually an equimolar ratio of amine and isocyanate groups, but the linear polymer was obtained with twofold molar excess of amine groups. Fullerenes change the network density, the share of the physical branching junctions and molecular

weight distribution (MWD) of the chain segments between the networking junctions. Additionally, molecular weight and the polydispersity index increase with C<sub>60</sub> concentration in the reaction blend. This evidences to a branching role of C<sub>60</sub> during their interaction with terminating amine groups. An influence of MWD of the chain segments between the networking junctions on tensile strength of the crosslinked and linear polymers was assumed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1431–1442, 2007

**Key words:** nanotechnology; nanomaterial; nanocomposite; polymer; TMA

## INTRODUCTION

Fullerenes<sup>1</sup> distributed uniformly in polymers widen the area of their use<sup>2</sup> despite the high cost of the commercial products. It is because the tensile strength, thermal stability, gas permeability, electrical conductivity, and resistance to ionizing radiation can change under their influence.<sup>3–8</sup> They are inhibitors of the thermal and thermooxidative degradation,<sup>9</sup> what is explained by interaction with macroradicals resulting in stable products.<sup>10</sup> By using functional polymers to react with fullerenes, or synthesizing polymers in the presence of fullerenes, various kinds of polymeric fullerenes can be prepared: side-chain polymers, main-chain polymers, dendritic fullerenes, star-shaped polymers, fullerene end-capped polymers, etc. Furthermore, by controlling the functional groups in polymer chains and reaction conditions, many well-defined fullerene polymers have been prepared.<sup>11</sup> After the discovery of a method to produce fullerenes in bulk quantities,<sup>12,13</sup> scientists start to study its chemistry.<sup>14,15</sup> One of the first reactions investigated was that between fullerenes and aliphatic amines.<sup>16</sup> Primary and secondary aliphatic amines add readily and repeatedly across full-

erenes. Tertiary aliphatic amines were soon thereafter shown to undergo photocycloadditions across them.<sup>17</sup> Despite the potentially rich chemistry available via reaction with aliphatic amines, a detailed understanding of the chemical and physical processes between them and fullerenes potentially influencing both chemical and super molecular structure of polymer composites was slow to develop. The nanoscale phase separation in polymer/fullerene bulk heterojunction composites requires the use of very sensitive new techniques for imaging, e.g., a high-resolution transmission electron microscope together with selected area electron diffraction, to visualize the polymer and fullerene distributions and their amorphous or crystalline organization in the film.<sup>18</sup> This was due to the difficulty in characterizing the complex product structure as well as a poor understanding of the reaction mechanisms involved.

The aim of present article is to study the effect of small additions of C<sub>60</sub> fullerenes (up to concentration  $C_{\text{ful}} = 10^{-6}$  mol/cm<sup>3</sup>) on molecular and topological structures and related properties of linear (pseudonetworked) and crosslinked polyester urethane ureas (PEUU).

## SYNTHESIS

A crosslinked PEUU was synthesized on the base of poly(oxypropylene) macrodiisocyanate (POPMDIC) and 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA,

Correspondence to: B. Jurkowski (Boleslaw.Jurkowski@put.poznan.pl).

**TABLE I**  
**Formulations of PEUU**

	Concentration (mol/cm <sup>3</sup> )		
	C <sub>60</sub> (10 <sup>7</sup> )	MOCA (10 <sup>4</sup> )	POPMDIC (10 <sup>4</sup> )
Linear	0.00	10.19	5.12
	1.17	10.23	5.09
	1.98	10.20	5.10
	3.72	10.22	5.10
	5.21	10.24	5.13
Crosslinked	0.00	5.59	5.56
	1.18	5.56	5.55
	1.95	5.57	5.58
	2.98	5.52	5.50
	4.81	5.54	5.53

Japan) with virtually an equimolar ratio of amine and isocyanate groups, but the linear polymer was obtained with twofold molar excess of amine groups. A given quantity of POPMDIC (Table I) was loaded into the vacuum reactor of the microturbo-mixer with glass chamber (manufactured in Institute of the Problems of Chemical Physics) and degassed while stirring at 1500 rpm at 70°C for 30 min. Next, C<sub>60</sub> fullerenes produced by OOO "BIT," Nizhnyi Novgorod, Russia, 99.98% purity dissolved in toluene were added to the POPMDIC. The mixture was stirred and the solvent was evacuated at a residual pressure of 0.1 mmHg during an hour. Then, the molten MOCA was added to the fully degassed reacting mass and the mixture was stirred for additional 1 min at 70°C with simultaneous evacuation of gases. Thus, the prepared reacting mass was put into the Teflon mold to make dumbbell specimens. Solidification was done at 130°C during 3 h.

## METHODS

The molecular and topological structures of PEUU were investigated by TMA;<sup>19,20</sup> PEUU with crosslinked structure was also studied by swelling in an aprotic tetrahydrofuran. A UIP-70M device made by the Central Design Bureau of the Russian Academy of Sciences (Moscow) has been used for thermomechanical analysis (TMA), following the procedure: the specimen was put into the measurement cell of the thermostatic chamber. The specimens, 2 mm in height and 1–5 mm in width, were cut from the plates of the PEUU. The surfaces of specimen contacting the base of the cell and the measuring probe with the hemispherical tip (its radius is 1 mm) should be parallel. The specimen was frozen without pressing at a scanning rate of about 4°/min, starting from room temperature, usually to –120°C. Next, the specimen was stored for 10–15 min to equalize thermal field within it. To obtain a thermomechanical curve (TMC), probe with a stable, but small load is moved down to contact the surface of the speci-

men, and heating at a scanning rate of about 4°C/min is provided. The TMA allows identifying several regions in a surface layer of polymers differing in linear thermal expansion coefficients. It also makes possible to evaluate the molecular-weight characteristic of the chain segments between junctions in individual regions. Simultaneously, evaluation of the compaction factor,  $V_c^{TMA} = 3(\alpha_2 - \alpha_1)T_g$ , could be done where  $\alpha_1$  is the coefficient of linear thermal expansion in a glassy state,  $\alpha_2$ —as  $\alpha_1$ , but in rubbery state. The  $V_c^{TMA}$  is related with polymer compactness.

The equilibrium swelling degree  $Q_\infty$  was used to estimate the crosslink density  $\nu_0$  (after the solvent had destroyed all the physical networking junctions) from the following equation, which was then compared with the results from the Cluff method in Ref. 21:

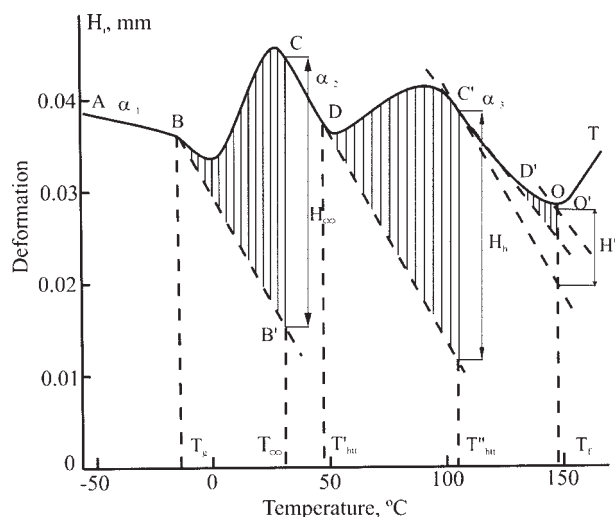
$$\nu_0 = 35.0 \times 10^{-4} / Q_\infty^2 [\text{mol/cm}^3] \quad (1)$$

where  $Q_\infty$  is the volumetric equilibrium of polymer swelling in a "good" solvent, which for polyurethane is TGF.

## RESULTS AND DISCUSSION

### Molecular and topological structures and properties of linear PEUU

The PEUU synthesized with a twofold excess of amine-groups in the presence of fullerenes was dissolvable in tetrahydrofuran. A thermomechanical curve of the PEUU synthesized without fullerenes is shown in Figure 1. It was taken over a temperature range between –100 and 200°C and is typical of a polymer with soft and rigid amorphous regions<sup>19,22,23</sup> with a pseudonetworked structure. Between –100 and –20°C, the polymer is in a glassy state, but it undergoes expansion while scanning tem-



**Figure 1** TMC for fullerenes-free linear PEUU.

perature (straight line AB), which is characterized by the linear thermal expansion coefficient  $\alpha_1 = 7.91 \times 10^{-5} \text{ deg}^{-1}$ .

At a temperature in point B, the expansion rate sharply increases (straight line BB'), which is indicative of the beginning of segmental relaxation in the polymer. At  $T_g = -20^\circ\text{C}$ , the lowest molecular weight (MW) polymer homologues between the networking junctions start to flow. The polymer undergoes deformation in the opposite direction owing to the fact that the probe tip penetrates the specimen. It is thermomechanical deformation of the polymer. That deformation occurs after the respective physical junctions in the network have broken down and polymer's elasticity modulus decreased. The flow processes take place at scanned temperature in the order of increasing MW of polymer homologues between the junctions what is followed by changes in deformation jumps. Their envelope forms a transitional zone in TMC (curve BC). For a given PEUU, this process terminates with the beginning of flow in the highest MW polymer homologue at  $T_\infty = 36^\circ\text{C}$  (point C in the TMC) and transition of polymers pseudonetworked structure to a thermally stable state—the plateau of high-elastic deformation (straight line CD).

The TMA allows determining simultaneously both MW of the chain segments between the junctions, which has undergone segmental relaxation by the moment of  $T_i$  ( $M_{ci}$ ) and the weight fraction of those chains ( $\phi_i$ ).<sup>19</sup> It means that the transitional zone in the TMC is a pseudointegral curve of MWD for the chain segments between the junctions of the pseudonetworked structure of the polymers amorphous region.

An analysis of this curve allows calculating the number-average  $\overline{M}_{cn} = 15.6 \text{ kg/mol}$  and weight-average molecular weight  $\overline{M}_{cw} = 21.0 \text{ kg/mol}$  for the chain segments between the junctions of the region's pseudonetwork and, consequently, the polydispersity index  $K = \overline{M}_{cw}/\overline{M}_{cn} = 1.38$ . An molecular weight distribution (MWD) for those chains is bimodal (Fig. 2, curve 1) and represent the distribution for the chain segments (as will be shown further) between the physical branching junctions.

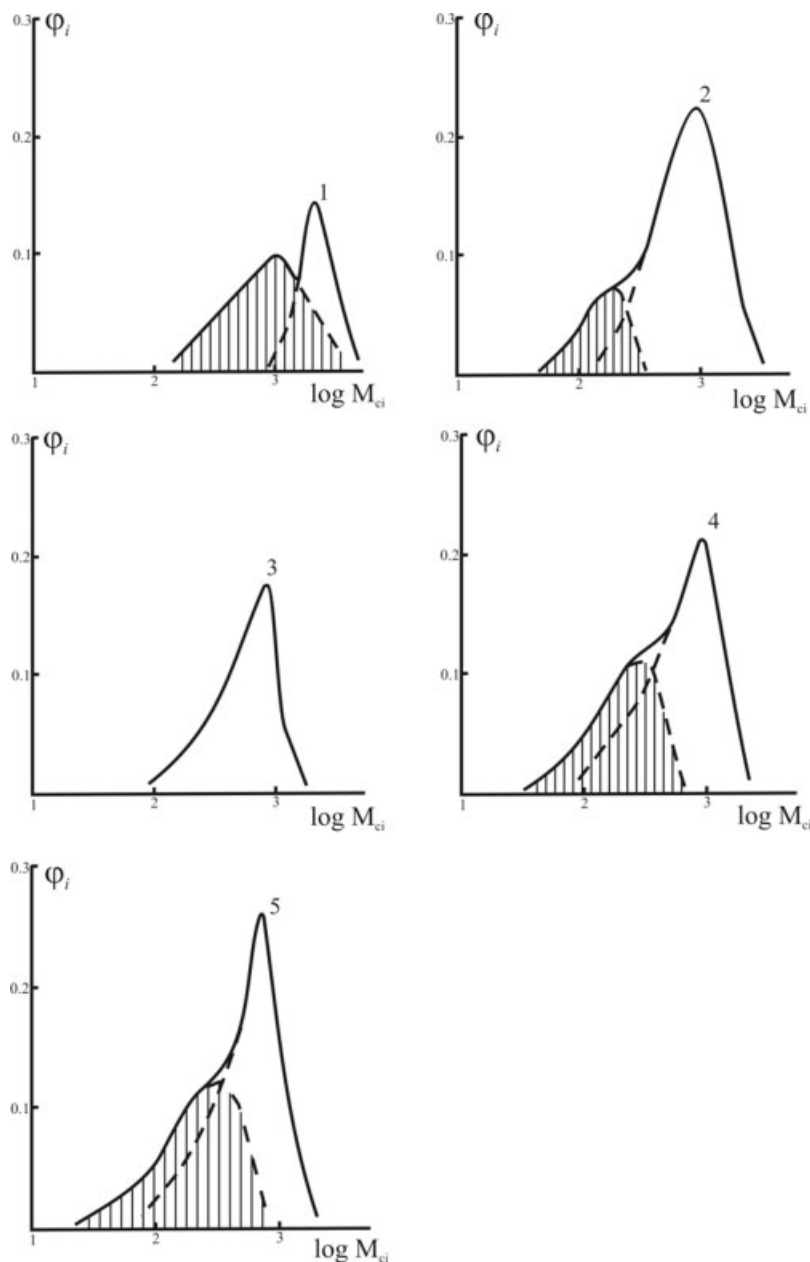
On being heated, the polymer expands in the region where the pseudonetworked structure is thermally stable, plateau of high elasticity—straight line CD, at the expense of increased volume of voids expressed by reciprocal of the compaction factor  $V_c^{\text{TMA}} = 3(\alpha_2 - \alpha_1)T_g^{\text{TMA}}$ ;  $\alpha_1$  is the coefficient of linear thermal expansion in a glassy state;  $\alpha_2$ , as  $\alpha_1$  but for a rubbery state, amorphous region  $\alpha_2 = 28.6 \times 10^{-5} \text{ deg}^{-1}$ . For the chain segments between the junctions of the amorphous region of a fullerenes-free PEUU,  $V_c^{\text{TMA}} = 0.157$ , the value typical of a rigid-chain polymer.

A thermally stable state of the pseudonetworked amorphous region is preserved up to point D. Above that temperature, the loaded at TMA test the polymer again undergoes thermomechanical deformation ( $H_i$ ), which indicates the beginning of new relaxation processes. At a temperature  $T'_{\text{htt}} = 49^\circ\text{C}$ , there starts a segmental relaxation in the chain segments between the junctions, most likely of cluster-type, of the first associative high-temperature amorphous region. Its appearance could be explained by different polarity along the chain causing formation of associates differing in interaction energies between neighboring segments. Here, a gradual transition to the flowing state of all polymer homologues in the order of increasing their molecular weight  $M_{c(h)i}$  is followed by a deformation jump  $\Delta H'_{(h)i}$ . Their envelope forms a transitional zone of the region (curve DC') with the same function of the pseudointegral curve, which was at segmental relaxation of the chain segments between the junctions in the amorphous region. It allows calculating the averaged molecular characteristics  $\overline{M}'_{cn(h)} = 10.6 \text{ kg/mol}$ ;  $\overline{M}'_{cw(h)} = 14.7 \text{ kg/mol}$ , and  $K = \overline{M}'_{cw(h)}/\overline{M}'_{cn(h)} = 1.39$  and the weight shares of chains of the region ( $\phi_h$ ).

The highest MW homologue of the first high-temperature region is transformed to the flowing state at temperature  $T''_{\text{htt}} = 106^\circ\text{C}$  corresponding to point C'. On heating PEUU above that temperature, it changes again to the rubbery state at a rate of  $\alpha_3 = 18.2 \times 10^{-5} \text{ deg}^{-1}$ . It is much lower than  $\alpha_2$ , which indicated that relaxation in the chain entanglements took place.<sup>19</sup> Their segmental relaxation, on increasing the temperature, start simultaneously with relaxation in the second associative (high-temperature) amorphous region. This relaxation is shown by the curve C'D'O' in the TMC. This curve is typical of the relaxation process in a single-region linear polymer.<sup>19</sup> An analysis of the transitional zone of TMC (curve D'O') allowed to determine characteristics of the structure of the second associative (high-temperature) amorphous region:  $\overline{M}''_{n(h)} = 9.1 \text{ kg/mol}$ ;  $\overline{M}''_{w(h)} = 11.7 \text{ kg/mol}$ ; and  $K = \overline{M}''_{w(h)}/\overline{M}''_{n(h)} = 1.38$ .

The weight content of PEUU chain segments in the structure of each topological region ( $\phi_a$ ,  $\phi'_h$ , and  $\phi''_h$ ) is directly proportional to their total thermomechanical deformation at the completion of relaxation ( $H_\infty$ ,  $H'_h$ , and  $H''_h$ ), being 0.45 : 0.33 : 0.22, respectively, for the amorphous and both associative (cluster-type) regions acting in it as the branching junctions. When averaged-over-regions MW of PEUU synthesized without fullerenes—assuming that the structure of each region is crossed once by chains—can be calculated using the equations:

$$M_w = \overline{M}_{cw} \times \phi_a + \overline{M}'_{cw(h)} \times \phi'_h + \overline{M}''_{w(h)} \times \phi''_h = 16.9 \text{ kg/mol}$$



**Figure 2** MWD for the chain segments between the junctions in linear PEUU with a pseudonetworked structure at fullerenes concentration  $C_{\text{ful}} \times 10^{-7}$  mol/cm<sup>3</sup>: (1) 0.00; (2) 1.17; (3) 1.98; (4) 3.72; and (5) 5.21, respectively.

$$M_n = \varphi_a / \bar{M}_{cn} + \varphi'_{(h)} / \bar{M}'_{cn(h)} + \varphi''_{(h)} / M''_{(h)} = 11.9 \text{ kg/mol}$$

$$K = M_w / M_n = 1.42.$$

The temperature at which PEUU begins to flow (point O') is  $T_f = 149^\circ\text{C}$ . It seems to coincide with the beginning of flow of the degradation products resulted from PEUU thermal degradation along urea bonds.

Addition of C<sub>60</sub> fullerenes in concentration between  $C_{\text{ful}} = 1.17$  and  $1.98 \times 10^{-7}$  mol/cm<sup>3</sup> to a reaction mass leads to formation of a polymer with

characteristics different from a fullerenes-free polymer (Table II). The structure of PEUU has almost identical averaged characteristics for the chain segments between the junctions. However, considerable changes were detected in MWD of the chain segments in the pseudonetworked structure of the amorphous region (Fig. 2). The said structure transforms from divided bimodality in fullerenes-free PEUU (curve 1) to a monomodal one (curve 3). This transformation of a pseudonetwork is related to the nature of the associative branching junctions. It is assumed that in linear fullerenes-free PEUU, a structure is formed with participation of two kinds of the



TABLE II  
Molecular and Relaxation Characteristics of Linear PEUU

Analyzed parameter <sup>a</sup> (95% confidence limit)	Concentration of fullerenes, $C_{\text{ful}}$ ( $10^7$ ) (mol/cm <sup>3</sup> )				
	0.00	1.17	1.98	3.72	5.21
Amorphous region					
$T_g$ (°C) ( $\pm 3-5$ )	-20	-22	-40	-35	-21
$T_\infty$ (°C) ( $\pm 3-5$ )	36	35	35	37	36
$\alpha_1$ ( $10^5$ ) deg <sup>-1</sup> ( $\pm 10\%$ )	7.93	8.80	8.50	8.56	9.69
$\alpha_2$ ( $10^5$ ) deg <sup>-1</sup> ( $\pm 10\%$ )	28.6	26.9	24.3	20.8	20.9
$V_c^{\text{TMA}}$ ( $\pm 10\%$ )	0.157	0.136	0.118	0.088	0.084
$\bar{M}_{cn}$ (kg/mol) ( $\pm 10\%$ )	15.6	15.6	16.1	16.0	14.8
$\bar{M}_{cw}$ (kg/mol) ( $\pm 10\%$ )	21.0	21.7	22.3	21.8	20.1
$K$ ( $\pm 10\%$ )	1.38	1.39	1.38	1.36	1.36
$v_e$ ( $10^4$ ) (mol/cm <sup>3</sup> ) ( $\pm 10\%$ )	0.71	0.71	0.68	0.69	0.74
$\phi_a$ ( $\pm 10\%$ )	0.45	0.50	0.58	0.57	0.53
First associative (high-temperature) amorphous region					
$T_{\text{htt}}^I$ (°C) ( $\pm 3-5$ )	49	86	89	-	-
$\bar{M}_{cn(h)}$ (kg/mol) ( $\pm 10\%$ )	10.6	6.5	2.5	-	-
$\bar{M}_{cw(h)}$ (kg/mol) ( $\pm 10\%$ )	14.7	8.6	3.1	-	-
$K$ ( $\pm 10\%$ )	1.39	1.32	1.25	-	-
$\phi_h^I$ ( $\pm 10\%$ )	0.33	0.26	0.07	0.00	0.00
Second associative (high-temperature) amorphous region					
$T_{\text{htt}}^{II}$ (°C) ( $\pm 3-5$ )	106	132	130	83	76
$\alpha_3$ ( $10^5$ ) (deg <sup>-1</sup> ) ( $\pm 10\%$ )	18.2	20.3	20.5	12.6	11.3
$M_{n(h)}^{II}$ (kg/mol) ( $\pm 10\%$ )	9.1	197.6	950.4	1648.5	1875.9
$M_{w(h)}^{II}$ (kg/mol) ( $\pm 10\%$ )	11.7	322.1	1606.2	2258.4	2485.4
$K$ ( $\pm 10\%$ )	1.38	1.63	1.69	1.37	1.33
$\phi_h^{II}$ ( $\pm 10\%$ )	0.22	0.25	0.35	0.43	0.47
$T_f$ (°C) ( $\pm 3-5$ )	149	177	178	154	151
Molecular weight averaged-over-regions					
$M_n$ (kg/mol) ( $\pm 10\%$ )	11.9	14.1	18.4	27.9	27.8
$M_w$ (kg/mol) ( $\pm 10\%$ )	16.9	102.4	575.3	983.6	1182.0
$K$ ( $\pm 10\%$ )	1.4	7.3	31.3	35.3	42.5

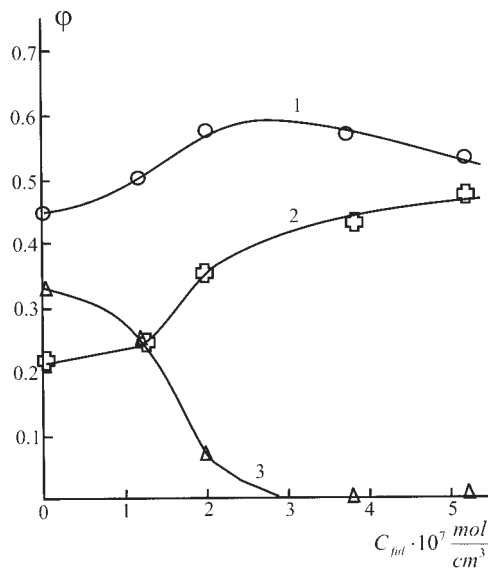
<sup>a</sup>  $M_w$ , the weight-average molecular weight between the junctions;  $M_n$ , the number-average molecular weight between the junctions;  $K = M_w/M_n$ , the polydispersity index;  $T_g$ , the glass-transition temperature;  $T_{\text{htt}}$ , the high-temperature transition;  $T_f$ , the temperature of the beginning of molecular flow;  $V_c^{\text{TMA}}$ , the compaction factor =  $3(\alpha_2 - \alpha_1)T_g^{\text{TMA}}$ ;  $\alpha_1$ , the coefficient of linear thermal expansion in a glassy state;  $\alpha_2$ , as  $\alpha_1$  but for a rubbery state, amorphous region;  $\alpha_3$  as  $\alpha_2$  but for an associative (high-temperature) region;  $\phi'$ , a weight share of amorphous region;  $\phi'' = 1 - \phi'$ , a weight share of a associative (high-temperature) amorphous region.

junctions. Concentration of the chain segments in them is virtually equal [Fig. 2(1)]—compare the relative share of shaded and not shaded parts in the spectrum. Introduction of fullerenes into the reaction mass results in lowering of concentration of the associative region. For  $C_{\text{ful}} = 1.17 \times 10^{-7}$  mol/cm<sup>3</sup>, concentration of the chain segments between the junctions in this region lowers till about 30% of the total amount of the chain segments [Fig. 2(2)]. For  $C_{\text{ful}} = 1.98 \times 10^{-7}$  mol/cm<sup>3</sup> the MWD of pseudonetworked structure is monomodal [Fig. 2(3)]; it means with a statistical distribution of the chain segments lengths between the junctions. Further increase in  $C_{\text{ful}}$  gives again a nonuniform pseudonetworked structure [Figs. 2(4–5)]. It seems to be resulted from fullerene-containing the branching junctions.

The fact that increased  $C_{\text{ful}}$  in a reaction mixture change a weight share of the chain segments  $\phi$  in

the regions (Fig. 3) is indicative of direct participation of fullerenes in formation of molecular structure of the polymer during synthesis. It also concerns participation in formation of chain segments' polarity owing to formation of different number of regions, from three for fullerenes concentration a little above  $C_{\text{ful}} = 1.92 \times 10^{-7}$  mol/cm<sup>3</sup> to two at higher concentrations. Simultaneously, varies interactions within the amorphous region. This is evidenced by changes in temperatures of the relaxation transitions ( $T_g$ ,  $T_{\text{htt}}^I$ ,  $T_{\text{htt}}^{II}$ ,  $T_f$ ) dependent on  $C_{\text{ful}}$  (Fig. 4).

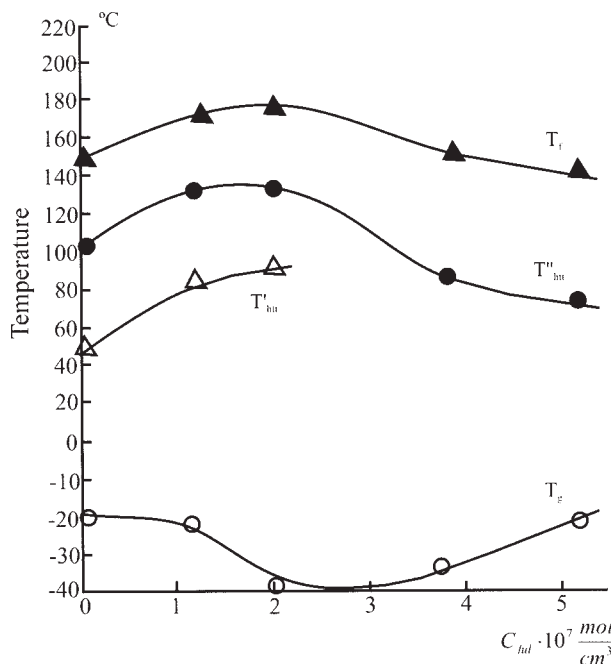
In PEUU, structure of the chain segments between the junctions of the amorphous region changes noticeably with increasing  $C_{\text{ful}}$ . The flexibility of the chains increases reaching a maximum at  $C_{\text{ful}} = 1.98 \times 10^{-7}$  mol/cm<sup>3</sup> for the most regular network. This is witnessed by decrease in the glass-transition temperature from  $-20^\circ\text{C}$  for a fullerenes-free polymer up to  $-40^\circ\text{C}$



**Figure 3** Relationship between region's weight share of linear PEUU and fullerenes concentration for (1) amorphous region; (2) first associative region; and (3) second associative region.

with its optimal concentration. Similarly to a change in  $T_g$ , a compaction factor  $V_c^{TMA}$  also changes (Table II). With the above optimal content of  $C_{60}$  fullerenes,  $V_c^{TMA} = 0.106$  value is typical of rubber-like chains.

At  $C_{ful} \geq 3.12 \times 10^{-7} \text{ mol/cm}^3$ , a topological structure with two regions is formed. The amorphous pseudonetworked region is formed with associative structures of high-melting region acting as the

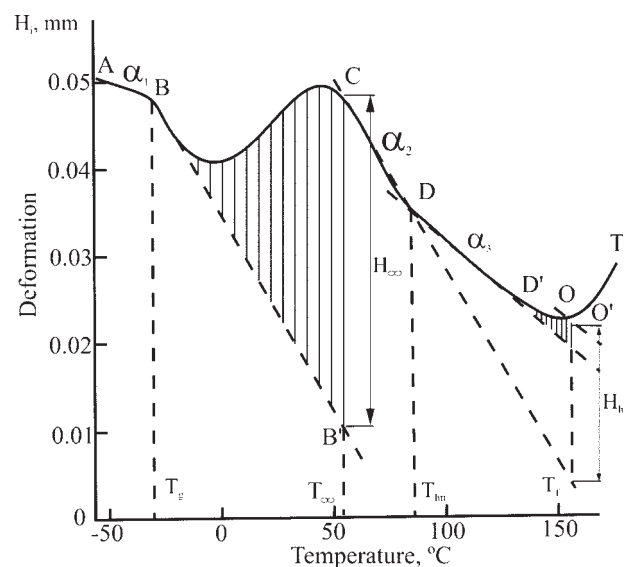


**Figure 4** Relationship between temperature of the relaxation transitions and  $C_{60}$  concentration of linear PEUU.

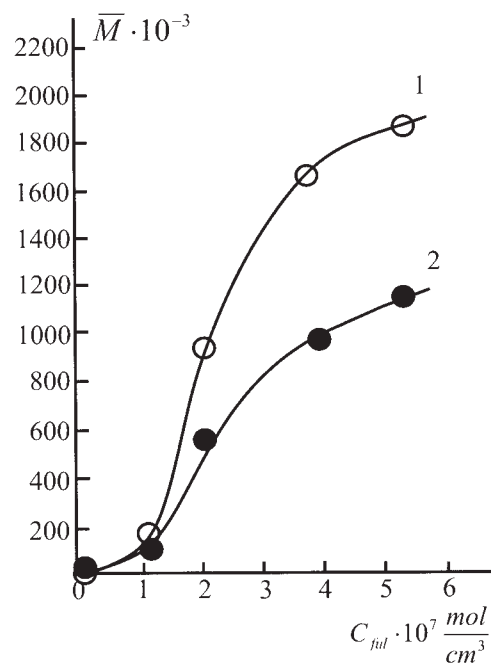
branching junctions. TMC for such polymers (with  $C_{ful} = 3.72 \times 10^{-7} \text{ mol/cm}^3$ ) is shown in Figure 5. Their characteristics are listed in Table II. Those data, together with earlier described results, give a picture of how  $C_{60}$  in a reaction mass influences the structure of PEUU.

There are two alternatives in the reaction of diamine with POPMDIC in the presence of  $C_{60}$  fullerenes: interaction with POPMDIC, or with  $C_{60}$ . A probability of them to give products of utterly different nature of the chains and a degree of interaction between the chains segments depend on the activation energy of these reactions. As no reliable kinetic data on this problem are available, we shall limit our comparison to an analysis of the results presented in this part of article with those discussed later.

Increase in  $C_{ful}$  in the reaction mixture change not only the chain's chemical structure, but also its molecular weight. Even at minimal  $C_{ful}$ , molecular weight of the chain segments in the second associative (high-temperature) region grows sharply. Figure 6 and Table II present the dependences of MW of chains in the structure of above-mentioned region and averaged-over-regions MW on  $C_{ful}$ . The relationship  $M''_{(h)} = f(C_{ful})$  has a clear S-like pattern that reflects a growth of dynamics for MW in the second associative region if fullerenes interacted with monomeric diamine. There it could be discriminated a stage with continuous increasing and, next, with decreasing the growth rate of  $M''_{(h)}$ . It could be resulted from interaction of fullerenes with macro-diamine.



**Figure 5** TMC for linear PEUU containing  $3.72 \times 10^{-7} \text{ mol/cm}^3$  of fullerenes.



**Figure 6** Relationship of the number-average molecular weight of the chain segments of the first associative region (1) and averaged-over-regions the weight-average molecular weight (2) of linear PEUU against fullerenes concentration.

A similar pattern was observed in the relationship of the weight-average MW of PEUU averaged-over-regions to  $C_{full}$  (Fig. 6, curve 2). As about 50 wt % of PEUU is a low MW fraction of the chain segments between the junctions of the amorphous region, the number-average molecular weight  $\bar{M}_{n(h)}$  does not exceed 28.0 kg/mol, and the MWD is polymodal. Variations in the polydispersity index is indicative of this fact (Table II).

A composite based on PEUU with a maximum growth rate for its MW that related with  $C_{full} = 1.98 \times 10^{-7} \text{ mol/cm}^3$  can be considered optimal as it corresponds to such structure, which mobility of the chain segments between the junctions in the pseudonet network of the amorphous region approaches that of rubbers ( $T_g = -40^\circ\text{C}$ ;  $V_c^{TMA} = 0.118$ ) for a maximum weight content of the region,  $\phi_a = 0.58$  (Table II).

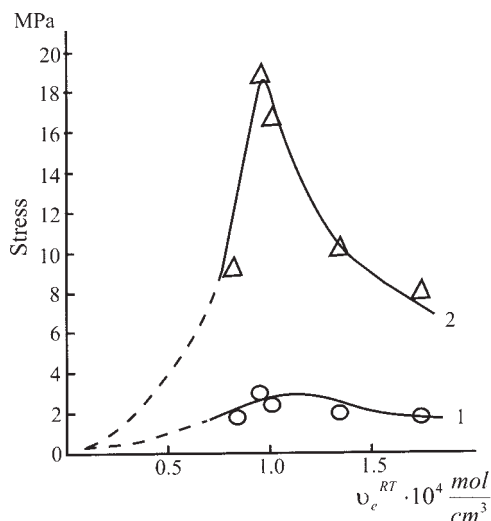
The mechanical tests performed at room temperature have proved the above supposition (Table III). However, a thermally stable state in the pseudonet networked structure (plateau of high elasticity) can be reached at much higher temperature ( $T_\infty = 36^\circ\text{C}$ ). At that temperature, some part of the high MW spectrum of the chain segments between the junctions has not undergone relaxation (flow condition has not been reached). Therefore, the parameters of PEUU pseudonet networked structure evaluated at scanned temperature at TMA test (Table II) do not correspond to those determined at room temperature. The crosslink density  $v_e$  for the same polymer depends on measurement method used and temperature, at which polymer is studied. It is constant if temperature is in the range corresponding to a plateau of high-elasticity. This range could be named as a zone of thermal stability of the polymer network. If the given temperature is lower than this, as is the case studied here, a part of high-molecular chain lengths spectrum is vitrified acting as the additional networking junctions and, as a result, the effective crosslink density is higher. Because of this, for comparison they should be recalculated to room temperature (RT). The product is listed in Table III as  $v_e^{RT}$ . Its value was obtained from TMC in the following way: in the result listening used in the regular calculating procedure<sup>19</sup> are excluded deformations related to the polymer homologues those till room temperature do not reach a flowing state. Next, all calculations are performed for the second time and new values of  $\bar{M}_{cn}$  and  $\bar{M}_{cw}$  are obtained, and from this  $1/\bar{M}_{cn} = v_e^{RT}$ .

The weakly pronounced is the extreme nature of a relationship between tensile strength and network density ( $v_e$ ) (Fig. 7). In the present case, it is rather determined by MWD of the chain segments between the junctions of the PEUU pseudonet networked structure. The extreme tensile strength and elastic modulus found at  $v_e = 1 \times 10^4 \text{ mol/cm}^3$  could not be explained as it was in literature,<sup>24</sup> but by the influence of fullerenes in concentration  $C_{full} = 2 \times 10^7 \text{ mol/cm}^3$  there giving the most regular monomodal MWD between the junctions of the polymer's pseudonet network.

**TABLE III**  
Characteristics of Linear PEUU

Fullerenes concentration ( $10^7$ ) ( $\text{mol/cm}^3$ )	Tensile strength (MPa)	Elastic modulus (MPa)	Elongation at break (%)	$v_e^{RT}$ a ( $10^4$ ) ( $\text{mol/cm}^3$ )
0.00	2.01	9.80	64.5	1.38
1.17	2.19	16.17	54.8	1.00
1.98	3.10	19.25	50.1	0.91
3.72	2.68	9.50	63.8	0.82
5.21	2.06	8.00	71.2	1.76

<sup>a</sup>  $v_e^{RT}$  means recalculated to room temperature



**Figure 7** Relationship of tensile strength (1) and elastic modulus (2) of linear PEUU against network density.

This agrees with a statistical distribution of the chain segments between the junctions, and hence with a maximum tensile strength. For the same reason, the elastic modulus is not directly proportional to the network density—as the high elasticity theory states<sup>25</sup>—but also influenced by distribution uniformity of their lengths.

### Effect of fullerenes on molecular and topological structures and properties of crosslinked PEUU

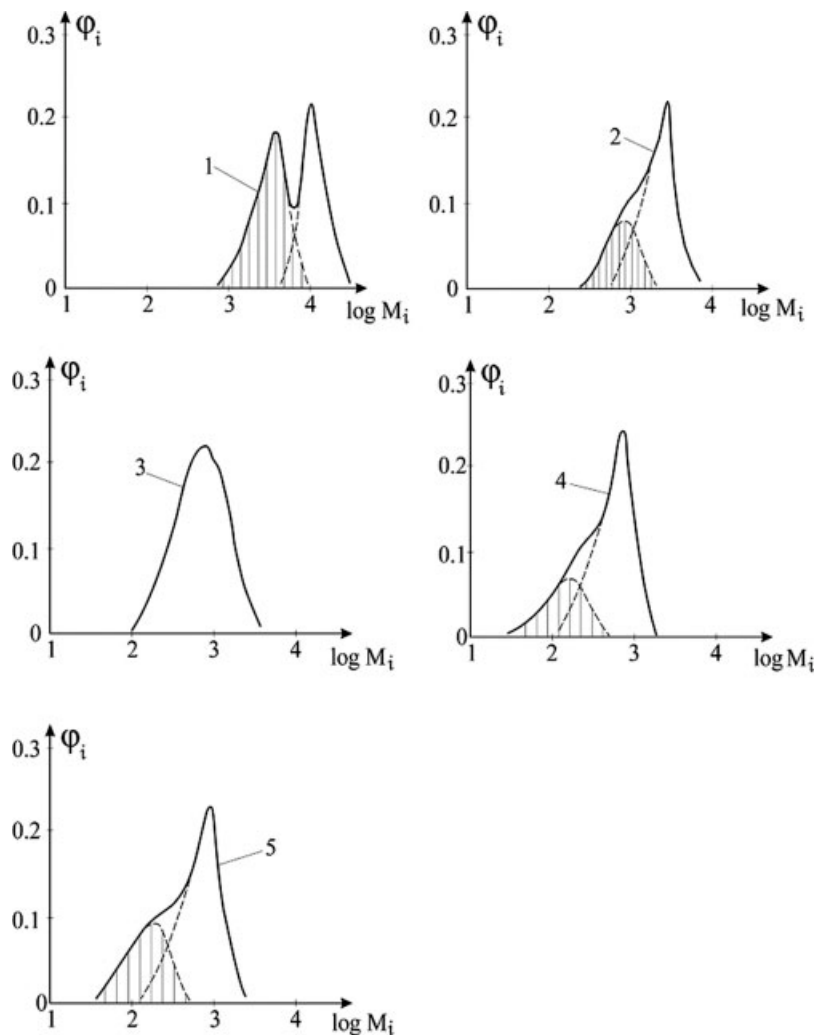
The role of the physical associative (cluster-type) junctions and crosslinks in polyurethane elastomers in formation of their molecular characteristics and tensile strength has been well understood.<sup>26</sup> For this class of polymers, the problem of crosslinks' structure differs from that for rubbers. It does not determine polymer properties. The use for synthesis of crosslinked PEUU the same components under the same regimes as in the case of making linear PEUU, will allow determination details of reaction of amine and POPMDIC in the presence of fullerenes. In addition, its influence on a polymer structure could be studied. The products of a reaction between diamine and POPMDIC in the presence of fullerenes have the crosslinked structure at equimolar ratios and linear structure at twofold excess of amine groups with reference to isocyanate groups. Investigation was performed by sol-gel analysis in an aprotic tetrahydrofuran. The TMC in Figure 5 is typical of both crosslinked and pseudonetworked polymers with a structure with two topological regions. The parameters describing a crosslinked PEUU are given in Table IV. Between  $-100$  and  $-65^\circ\text{C}$ , the polymer is in the glassy state (straight line AB) and is characterized by a coefficient of linear thermal expansion  $\alpha_1$

**TABLE IV**  
Molecular Relaxation Characteristics of Topological Structure in Crosslinked PEUU Containing  $\text{C}_{60}$

Analyzed parameter <sup>a</sup> (95% confidence limit)	Fullerenes concentration ( $10^7$ ) (mol/cm <sup>3</sup> )				
	0.00	1.18	1.95	2.98	4.81
<b>Amorphous region</b>					
$T_g$ ( $^\circ\text{C}$ ) ( $\pm 3-5$ )	-65	-24	-20	-34	-37
$\alpha_1$ ( $10^5$ ) deg <sup>-1</sup> ( $\pm 10\%$ )	4.94	5.95	6.24	4.69	5.12
$\alpha_2$ ( $10^5$ ) deg <sup>-1</sup> ( $\pm 10\%$ )	26.7	27.8	27.32	23.3	24.7
$\bar{M}_{cn}$ (kg/mol) ( $\pm 10\%$ )	1.49	0.83	0.74	0.58	0.49
$\bar{M}_{cw}$ (kg/mol) ( $\pm 10\%$ )	2.21	1.15	1.00	0.93	0.68
$K$ ( $\pm 10\%$ )	1.49	1.40	1.35	1.40	1.41
$V_c^{\text{TMA}}$ ( $\pm 10\%$ )	0.141	0.159	0.160	0.133	0.139
$v_e$ ( $10^4$ ) (mol/cm <sup>3</sup> ) ( $\pm 10\%$ )	6.71	12.05	13.51	17.24	20.41
$\phi_a$ ( $\pm 10\%$ )	0.68	0.66	0.75	0.87	0.85
<b>Associative (high-temperature) region</b>					
$T_h$ ( $^\circ\text{C}$ ) ( $\pm 3-5$ )	66	76	95	111	123
$\alpha_3$ ( $10^5$ ) (deg <sup>-1</sup> ) ( $\pm 10\%$ )	9.88	16.7	20.0	21.1	21.6
$M_{n(h)}$ kg/mol ( $\pm 10\%$ )	1230.0	941.9	502.0	183.2	56.0
$M_{w(h)}$ kg/mol ( $\pm 10\%$ )	1704.5	1256.3	662.6	244.6	78.9
$K$ ( $\pm 10\%$ )	1.39	1.33	1.32	1.39	1.41
$\phi_h$ ( $\pm 10\%$ )	0.32	0.34	0.25	0.13	0.15
$T_f$ ( $^\circ\text{C}$ ) ( $\pm 3-5$ )	160	165	167	158	161
<b>Swelling</b>					
$Q_\infty$ ( $\pm 10\%$ )	3.52	3.67	3.55	3.77	3.42
$W_s$ ( $\pm 10\%$ )	0.015	0.017	0.016	0.019	0.015
$v_Q$ ( $10^4$ ) (mol/cm <sup>3</sup> ) ( $\pm 10\%$ )	2.82	2.60	2.70	2.76	2.99
$\phi_{ph}$ ( $\pm 10\%$ )	0.58	0.78	0.80	0.84	0.85

<sup>a</sup> For description see Table II;  $\phi_{ph}$  is a share of the physical branching junctions.





**Figure 8** MWD for the chain segments between the junctions in crosslinked PEUU containing fullerenes  $\times 10^{-7}$  mol/cm<sup>3</sup> (1) 0.00; (2) 1.18; (3) 1.95; (4) 2.98; (5) 4.81, respectively.

$= 4.94 \times 10^{-5} \text{ deg}^{-1}$ . At a temperature in point B ( $T_g = -65^\circ\text{C}$ ), segmental mobility of the chain segments between the junctions of the PEUU network begins to devitrify. It is accompanied by a sharp increase in the expansion rate (dilatometric straight line BB') and thermomechanical deformation  $H_i$  (penetration of the probe tip into the polymer). This deformation results from lowering in the modulus of crosslinked polymer during gradual devitrification of segmental mobility and transition to the flowing state of homologues between the junctions of every MW from the shortest one like Kuhn segment at  $T_g$  region to the highest one at  $T_\infty$ . On reaching a flow temperature by each polymer homologue with molecular weight  $M_{ci}$ , a deformation jump ( $\Delta H_i$ ) occurs, whose envelope forms a transitional zone in the TMC (curve BC).

The abscissa of a curve for a transitional zone ( $T_i - T_g$ ) is directly proportional<sup>19</sup> to  $M_{ci}$ ; the ordinate, to a weight share  $\varphi_i$  of those homologues ( $\varphi_i = \Delta H_i /$

$H_\infty$ , where  $H_\infty$  is the total thermomechanical deformation at temperature  $T_\infty$ ). These are known to be coordinates of a MWD integral curve. In the present case, it is for the chain segments between the junctions in a crosslinked polymer. By its analysis, the number-average ( $\overline{M}_{cn}$ ) and weight-average ( $\overline{M}_{cw}$ ) molecular weight for PEUU chain segments between the junctions could be found. They are, respectively,  $\overline{M}_{cn} = 1.49$  kg/mol;  $\overline{M}_{cw} = 2.21$  kg/mol; and  $K = 1.49$ . Their MWD (Fig. 8) is bimodal and illustrates the effect of two types of the branching junctions, i.e., crosslinks and associative ones, on PEUU network formation.

At a temperature in point C ( $T_\infty = 29^\circ\text{C}$ ), segmental relaxation is completed in the highest-MW homologues and the crosslinked structure becomes thermally stable—elasticity plateau (straight line CD). In this region, like in the pseudonetworked structure in a linear PEUU, the polymer expands at the expense of increased volume of all voids including the free

volume at a constant rate for which the coefficient of linear thermal expansion  $\alpha_2 = 26.7 \times 10^{-5} \text{ deg}^{-1}$ . Consequently, at the glass-transition temperature  $V_c^{\text{TMA}} = 0.141$  in the structure of amorphous region and is witnessing for the rigid-chain nature of the chain segments between the junctions.

The region of thermal stability of the crosslinked structure in a fullerenes-free PEUU terminates at a temperature of  $66^\circ\text{C}$  (point D). Heating above this temperature decreases sharply its expansion rate because there starts a process of segmental relaxation of previously associated segments of the chains in the high-temperature topological region. During relaxation, the expansion rate of the polymer is constant, and  $\alpha_3 = 9.88 \times 10^{-5} \text{ deg}^{-1}$ . The lowest MW homologue begins to flow at a temperature corresponding to point D'. Gradually, flow of all the higher MW homologues forms a transitional zone in a TMC fragment describing relaxation in the above-mentioned region (curve D'O'). With an assumption that at a temperature corresponding to point O ( $T_f = 160^\circ\text{C}$ ) begins not only molecular flow of products resulting from thermal decomposition of crosslinks (biuret and urethane groups in PEUU), but also associative structures of the high-temperature region, we have calculated their molecular characteristics:

$$M''_{n(h)} = 1.23; \text{ kg/mol}; \quad M''_{w(h)} = 1.70 \text{ kg/mol};$$

and  $K = 1.39$ .

The weight share of the chain segments between the junctions of amorphous and associative (high-temperature) regions are proportional to the height of TMC those equals  $H_\infty$  and  $H_h$  as a ratio of 0.68:0.32, respectively.

Swelling of fullerenes-free PEUU, up to equilibrium ( $Q_\infty = 3.52$ ) broke down the structure of the high-temperature region, which allowed calculating molecular characteristics of the chain segments between crosslinks ( $v_Q$ ):

$$v_Q = 35 \times 10^{-4} / Q_\infty^2 = 2.82 \times 10^{-4} \text{ mol/cm}^3$$

and  $\bar{M}_{cn} = 3.55 \text{ kg/mol}$ .

The share of the physical junctions in its network at room temperature  $\phi = 1 - v_Q/v_e = 0.58$ .

The number of topological regions of PEUU, synthesized at every  $C_{\text{ful}}$  tested, is the same as without fullerenes. However, their characteristics are different (Table IV). Fullerenes influence the structure of crosslinked PEUU in a complex manner. It implies fullerenes participation in formation of both associative (high-temperature) and nonassociative (local) the branching junctions of the polymers' crosslinked structure. The latter could act as a "plasticizing" structure, thus preventing formation of a high-

temperature region. This fact is proved by the fact that amount of this region drops with increasing  $C_{\text{ful}}$  and stabilizes at a twice as small value as that of neat (fullerenes-free) PEUU.

Simultaneously, with decrease in the amount of associated chains, their molecular weight ( $M_{n(h)}$ ) also decreases, but the energy for interaction between the chains in the region's structure rises significantly. This is shown in increase of temperature at which segmental relaxation starts in the region's structure ( $T_{\text{htt}}$ ) as well as in this process rate that expressed by the coefficient of thermal change in linear dimensions during melting ( $\alpha_3$ ).

Considerable changes in the crosslinked structure of the amorphous region also take place in a presence of fullerenes. Besides crosslinks, two more types of the physical branching junctions appear with fullerenes participation in the reaction mixture. This increases significantly the effective crosslink density in PEUU. With a maximum concentration,  $C_{\text{ful}} = 4.81 \times 10^{-7} \text{ mol/cm}^3$ , the number-average MW of PEUU for the chain segments between the junctions drops threefold. The MWD of chain segments between the junctions for PEUU amorphous region also varies (Fig. 8). Here similar processes are observed as described for linear PEUU (Fig. 2).

In the presence of  $C_{60}$  fullerenes (Table IV), there is formed a PEUU crosslinked structure with different interaction energy of the chain segments between the junctions depending on  $C_{\text{ful}}$ . From the viewpoint of influence of fullerenes on the chains molecular mobility, its concentration  $C_{\text{ful}} = 1.95 \times 10^{-7} \text{ mol/cm}^3$  is optimal. At this concentration,  $T_g = -20^\circ\text{C}$  at which  $V_c^{\text{TMA}} = 0.160$ . For all of the remaining composites, these parameters correspond to less rigid chain state in segments between the junctions of PEUU network.

Swelling of PEUU in aprotic tetrahydrofuran up to equilibrium  $Q_\infty$  when breaks down all of the physical branching junctions in the network, make possible to determine the network density, but only between crosslinks ( $v_Q$ ) (Table IV). These values are independent of  $C_{\text{ful}}$ , which is indicative that  $C_{60}$  fullerenes do not participate in crosslinking.

It is supposed that the role of fullerenes is to break down the polymer associative (cluster type) structures and form the local physical branching junctions at the expense of fullerenes interaction with terminating amine groups. With a stoichiometric ratio of amine and isocyanate groups in the initial blend of components, when the latter undergo a side reaction with the product of the primary reaction (urea)—a part of amine groups remain unreacted. These groups could interact physically with  $C_{60}$  fullerenes leading to creation of two or three functional junctions<sup>27</sup> thus forming additionally a PEUU pseudonet- work. A relative share of those junctions, together

TABLE V  
Effect of Fullerenes on Properties of Crosslinked PEUU

Concentration of $C_{60}$ ( $10^7$ ) (mol/cm <sup>3</sup> )	$v_e^{RT}$ ( $10^4$ ) (mol/cm <sup>3</sup> )	Tensile strength (MPa)	Elastic modulus (MPa)	Elongation at break (%)	Breaking work <sup>a</sup> (J)
0.0	6.71	26.6	32.8	482	16.2
1.18	12.05	32.4	46.5	580	23.3
1.95	14.29	35.1	57.5	590	25.0
2.98	17.24	32.9	55.5	340	20.2
4.81	20.41	30.1	43.4	323	18.8

<sup>a</sup> Breaking work is the area below a stress–deformation curve.

with associative ones, in their total concentration has been calculated by comparing  $v_e$  (from TMA) and  $v_Q$  (from equilibrium swelling). It rises from 0.58 for a fullerenes-free PEUU with tendency to reach a maximum 0.84–0.85 at about  $C_{\text{ful}} = 2 \times 10^{-7}$  mol/cm<sup>3</sup>.

The results of mechanical tests of linear and crosslinked PEUU are presented in Table V. In addition, tensile strength and elastic modulus are shown against  $v_e$  that reduced to room temperature (Fig. 9). An extreme nature of how tensile strength depends on crosslink density is typical of crosslinked and pseudonetworked polymers. The explanation of this phenomenon could be the same as above for linear PEUU (Fig. 7).

As for similar elastic modulus relationship, a determinant factor for an extreme pattern of this dependence appear not only crosslinking, but also a network structure, particularly, the nature of MWD of the chain segments between the junctions in PEUU's amorphous region and the polydispersity index. A similar influence of distribution regularity

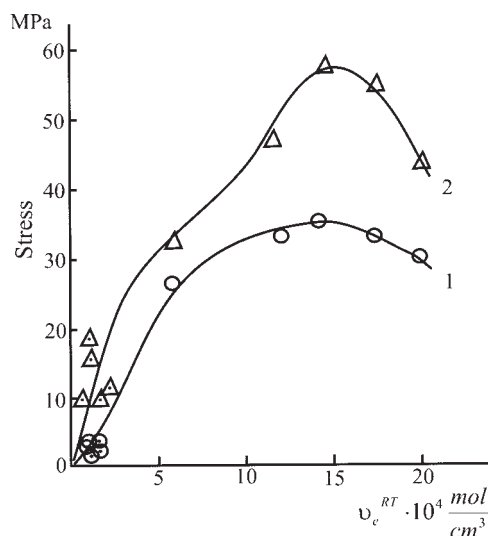


Figure 9 Relationship of tensile strength (1) and elastic modulus (2) of crosslinked PEUU against fullerenes concentration (points inside triangles and circle means values for linear PEUU).

by lengths of the chain segments between the junctions could be for the tensile strength. Both tensile strength and elastic modulus for the linear and crosslinked polymers are located on the same dependence that evidence that they are independent on a nature of the branching junctions. However, the time factor influencing the specimen deformation should not be forgotten for polymers with a pseudo-networked structure.

## CONCLUSIONS

1. Interaction of POPMDIC with diamine, with two-fold excess of the latter, in the presence of  $C_{60}$  fullerenes increase MW and the polydispersity index with fullerene concentration in the reaction mixture. This evidences to a branching role of fullerenes during their interaction with terminating amine groups.
2. The topological structure of linear PEUU synthesized without  $C_{60}$  fullerenes has three topological regions. If  $C_{60}$  is introduced into the blended reactive components, MW of PEUU grows, and simultaneously molecular-relaxation characteristics in all of the topological regions are changed. Their number remains unchanged only at  $C_{\text{ful}} < 2 \times 10^{-7}$  mol/cm<sup>3</sup>.
3. With higher concentration of fullerenes, the topological structure of linear PEUU transforms from three regions to a two regions one. The pseudo-networked structure of the amorphous region is formed by the branching junctions of the high-temperature associative cluster-type region. For  $C_{\text{ful}} \leq 5.2 \times 10^{-7}$  mol/cm<sup>3</sup> at unchanged degree of structure forming in the amorphous region, mobility of the chain segments between the junctions of the network (influencing on  $T_g^{\text{TMA}}$  and  $V_c^{\text{TMA}}$ ) and amount of the region is extremely in nature. The molecular weight of chains' segments in the structure of the high-temperature region and its amount grew continuously with  $C_{60}$  concentration. Also, extreme changes in the thermal stability expressed by  $T_f^{\text{TMA}}$  of linear PEUU, which

reaches a maximum at  $C_{\text{ful}} = 2 \times 10^{-7}$  mol/cm<sup>3</sup>, were observed.

4. Interaction of POPMDIC and diamine at equimolar ratio of the components, with C<sub>60</sub> fullerenes or without it, gives a crosslinked PEUU that has chemical and physical associative the branching junctions. The presence of C<sub>60</sub> fullerenes does not influence on the chemistry of the primary reactions between amine and isocyanate groups. However, it participates in forming the local physical branching junctions, but disturbs creation of the associative cluster-type branching junctions.
5. At optimal fullerenes concentration, a structure having a unimodal MWD of the chain segments between the junctions is formed. This concentration is the same for both pseudonetworked and crosslinked PEUU.
6. The extreme character of variations in elastic modulus and tensile strength with the network density for both linear and crosslinked PEUU could be explained not only by the crosslinking, but also by the pattern of MWD of the chain segments between the branching junctions.

## References

1. Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. F. *Nature* 1985, 318, 162.
2. Karpacheva, G. P. *Vysokomol Soed (High-Molecular Weight Compounds) Ser C* 2000, 42, 1974.
3. Shibaev, L. A.; Antonova, T. A.; Vinogradova, L. V.; Ginsburg, B. M.; Zgonnik, V. N.; Melenevskaya, E. Y. *Letters to Zh T Ph* 1997, 23, 81.
4. Troitskii, B. B.; Troitskaya, L. S.; Yakhnov, A. S.; Lopatin, M. A.; Novikova, M. A. *Eur Polym J* 1997, 33, 1587.
5. Troitskii, B. B.; Troitskaya, L. S.; Jakhov, A. S.; Dmitriev, A. A.; Denisova, V. N.; Novikova, M. A.; Domrachev, G. A.; Anikina, L. I.; Doklady, A. N. *Rep Russ Acad Sci* 1998, 363, 79.
6. Troitskii, B. B.; Troitskaya, L. S.; Dmitriev, A. A.; Yakhnov, A. S. *Eur Polym J* 2000, 36, 1073.
7. Troitskii, B. B.; Domrachev, G. A.; Khokhlova, L. V.; Anikina, L. I. *Vysokomol Soed (High-Molecular Weight Compounds) Ser A* 2001, 43, 1540.
8. Jurkowska, B.; Jurkowski, B.; Kamrowski, P.; Pesetskii, S. S.; Koval, V. N.; Pinchuk, L. S.; Olkhov, Y. A. *J Appl Polym Sci* 2006, 100, 390.
9. Zuev, V. V.; Bertini, F.; Audisio, G. *Polym Degrad Stab* 2005, 90, 28.
10. Troitskii, B. B.; Domrachev, G. A.; Davydov, A. I.; Zhogova, K. B.; Doklady A. N. *Rep Russ Acad Sci* 2002, 387, 510.
11. Wang, C.; Guo, Z.-X.; Fu, S.; Wu, W.; Zhu, D. *Prog Polym Sci* 2004, 29, 1079.
12. Kratschmer, W.; Fostiropoulos, K.; Huffman D. R. *Chem Phys Lett* 1990, 170, 167.
13. Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* 1990, 347, 354.
14. Hirsch, A. *The Chemistry of Fullerenes*; Thieme: New York, 1994.
15. Prato, M. *J Mater Chem* 1997, 7, 1097.
16. Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P.-M.; Koch, H. E.; Srdanov, G.; Webb, H. M. In *Fullerenes: Synthesis, Properties and Chemistry of Large Carbon Clusters*, ACS Symposium Series; Hammond, G. S., Kuck, V. J., Eds.; ACS: Washington, DC, 1992; Vol. 48, Chapter 11, pp 161–175.
17. Lawson, G. E.; Kitaygorodskiy, A.; Ma, B.; Bunker, C. E.; Sun, Y.-P. *J Chem Soc Chem Commun* 1995, 2225.
18. Hoppe, H.; Drees, M.; Schwinger, W.; Schaffler, F.; Sariciftcia, N. S. *Synth Met* 2005, 152, 117.
19. Olkhov, Y. A.; Jurkowski, B. *J Therm Anal Cal* 2005, 81, 489.
20. Jurkowska, B.; Jurkowski, B.; Olkhov, Y. A. *J Therm Anal Cal* 2005, 81, 27.
21. Olkhov, Y. A.; Kalmikov, Y. B.; Baturin S. M. *Vysokomol Soed (High-Molecular Weight Compounds) Ser A* 1984, 26, 1681.
22. Chen, W.; Wunderlich, B. *Macromol Chem Phys* 1999, 200, 283.
23. Wunderlich B. *J Therm Anal Cal* 2004, 78, 7.
24. Dogadkin, B. A.; Karmin, B. K. *Kolloid Zh* 1947, 9, 348.
25. Ferry, G. J. *Viscoelastic Properties of Polymers*; Foreign Literature Publishers: Moscow, 1963; p 216. (Russian translation).
26. Wright, P.; Camming, A. *Polyurethane Elastomers*; Khimia Publishers: Leningrad, 1973; p 200. (Russian translation).
27. Goldshleger, N. A.; Lobach, A. S.; Astakhova, A. S.; Kaplunov, M. G.; Kulikov, A. V.; Moravskii, A. P.; Roshechupkina, O. S.; Snulga, Y. M.; *Izvestia, A. N. Trans Russ Acad Sci Chem Ser* 1994, 6, 1143.