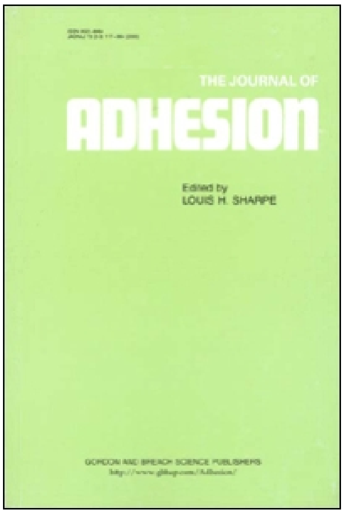

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Structure-Property Relationships in Thermoplastic Pseudo-Interpenetrating Polymer Networks. I. Phase Morphology

L. M. Sergeeva[a]; O. P. Grigoryeva[a]; O. N. Zimich[a]; E. G. Privalko[a]; V. I. Shtompel[a]; V. P. Privalko[ab]; P. Pissis[b]; A. Kyritsis[b]
[a] Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine [b] National Technical University of Athens, Zografou Campus, Athens, Greece

To cite this Article Sergeeva, L. M. , Grigoryeva, O. P. , Zimich, O. N. , Privalko, E. G. , Shtompel, V. I. , Privalko, V. P. , Pissis, P. and Kyritsis, A.(1997) 'Structure-Property Relationships in Thermoplastic Pseudo-Interpenetrating Polymer Networks. I. Phase Morphology', The Journal of Adhesion, 64: 1, 161 — 171

To link to this Article: DOI: 10.1080/00218469708010537

URL: http://dx.doi.org/10.1080/00218469708010537

J. Adhesion, 1997, Vol. 64, pp. 161–171
Reprints available directly from the publisher
Photocopying permitted by license only

Structure-Property Relationships in Thermoplastic Pseudo-Interpenetrating Polymer Networks. I. Phase Morphology*

L. M. SERGEEVA[a], O. P. GRIGORYEVA[a], O. N. ZIMICH[a],
E. G. PRIVALKO[a], V. I. SHTOMPEL[a], V. P. PRIVALKO[a,**,b],
P. PISSIS[b] and A. KYRITSIS[b]

[a]*Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, 253160 Kyiv, Ukraine;*
[b]*National Technical University of Athens, Zografou Campus, 15780 Athens, Greece*

(Received 30 December 1996; In final form 18 March 1997)

Pseudo-thermoplastic interpenetrating polymer networks (p-TIPNs) prepared by mechanical mixing of a crystallizable polyurethane (CPU) and styrene/acrylic acid random copolymer (S/AA) were characterized by specific heat capacity measurements in the temperature interval 133–433 K, as well as by wide-angle and small-angle X-ray scattering. It was established that:

1. Crystallizability of BAG is the main cause of microphase-separated morphology of CPU.
2. Limited miscibility of CPU with S/AA significantly affects the phase morphology of p-TIPNs on their base. Mixed microphase of fixed composition [CPU/(S/AA) = 90/10] and essentially pure microphase of S/AA are the main structural entities in as-quenched samples of p-TIPNs of whatever nominal composition. More complex phase morphology (that is, coexistence of essentially pure microphases of crystallized BAG and of S/AA, and of the mixed CPU/(S/AA) microphase enriched with S/AA) is expected for initial samples.

Keywords: Crystallizable polyurethane; random copolymer; pseudo-interpenetrating polymer networks; phase morphology

---

*One of a Collection of papers honoring Yuri S. Lipatov on the occasion of his 70th birthday, 10 July 1997.

**Corresponding author.

INTRODUCTION

In broad terms, interpenetrating polymer networks (IPNs) may be defined as binary polymer systems, in which at least one component is crosslinked to avoid the incipient phase separation [1,2]. A relatively recent addition to this class of materials are the "thermoplastic" IPNs (TIPN). In a strict sense, reference ot these latter systems as IPNs can be somewhat misleading, in so far as, in contrast to classical IPNs, neither of their components is chemically crosslinked. Nevertheless, it is believed that spatial networks do exist in TIPNs, with strong "physical" bonds (like ionic and hydrogen bonds) and/or microcrystallites playing the role of effective crosslinking sites. Thus, TIPNs are expected to behave essentially as chemically-crosslinked polymers, or as thermoplastics in the low-and high-temperature domains, respectively.

Depending on the method of preparation, one should distinguish between "mechanically-blended" and "chemically-blended" TIPNs. The former are prepared by mechanical mixing of components either in the melt state, or in a common solvent, whereas the latter are produced by a matrix polymerization technique. It is the mechanically-blended, pseudo-TIPNs (p-TIPNs) of a crystallizable polyurethane (CPU) and of a styrene/acrylic acid copolymer (S/AA) which are the objects of the present study (the prefix "pseudo" is intended to specify these TIPNs as precursors of "true" TIPNs which can be obtained by subsequent ionization of carboxylic groups). Results of preliminary characterization of these systems by dynamic mechanical analysis, water uptake, specific electrical resistance and ultimate mechanical properties were reported elsewhere [3].

EXPERIMENTAL

Materials

CPU was prepared by the reaction (3 hours at 348°K) of toluene diisocyanate, TDI (mixture of 2,4- and 2,6-isomers, molar ratio 65/35), with oligomeric butylene adipate glycol, BAG (molar mass 2000), in 70% solution of ethyl acetate (molar proportion of reagents 1.01/1.00, catalyst: tin dibutyl laurate, 0.2 wt.%).

S/AA was obtained by the bulk radical copolymerization (6 hours at 343°K) of styrene and acrylic acid (molar ratio 75/25, initiator: benzoyl peroxide, 0.3 wt.%) in nitrogen flux. Composition homogeneity was ensured by arresting the reaction at the transformation degree about 70%. The reaction product was dissolved in methanol, precipitated by water, filtered and vacuum-dried. The molar ratio of comonomers in S/AA was, approximately, 72/28 (estimated from carboxylic group content by base titration [4]).

Molar masses determined by DuPont Liquid Chromatograph were the following: $\langle M_w \rangle = 115000$, $\langle M_w \rangle = 43000$ (CPU); $\langle M_w \rangle = 127000$, $\langle M_n \rangle = 55000$ (S/AA).

Thin films of p-TIPNs of different compositions were prepared by casting from 20%-solutions in dioxane onto Teflon$^{\text{TM}}$ plates and subsequent evacuation to constant weight.

Methods

Specific heat capacity (c_p) was measured in the temperature interval 133–433°K by a home-made differential calorimeter with diathermal sheels [5] (heating rate about 2 deg/min, mean experimental error below 3%).

Wide-angle and small-angle X-ray scattering (WAXS and SAXS) curves were recorded by X-ray diffractometers DRON-4-07 and KRM-1, respectively (Cu-K_α radiation monochromatized by Ni filter). Mean crystallite dimensions $\langle D \rangle$ and the degree of crystallinity $\langle X \rangle$ of BAG were estimated by the methods of Scherer and Mattews, respectively; "long periods" (*i.e.*, mean distances between centers of crystallites, $\langle L \rangle$) were calculated by the Wulff-Braggs equation [6, 7].

RESULTS AND DISCUSSION

Calorimetry

The most prominent features of the first heating run of initial (as-cast) samples of CPU are the relatively small Δc_{p1} jump at the glass transition temperature of the amorphous phase ($T_{g1} = 234°\text{K}$), and the large melting endotherm of BAG microcrystals with a peak at the melting point, $T_m = 325°K$ (solid line in Fig. 1a). In the second heating run of the same sample quenched from the melt in liquid nitrogen (broken line in Fig. 1a), one observes the shift of T_{g1} to lower temperatures and the corresponding increase of Δc_{p1}, which can be readily explained by removal of constraints from BAG microcrystals on the mobility of amorphous material of CPU. The observed $T_{g1} = 218°K$ for the quenched CPU is very close to the reported T_g of an individual BAG [8].

The exothermal peak above T_g of quenched CPU (Fig. 1a) can be attributed to the "cold crystallization" of BAG; judging by a decreased area of the melting endotherm, the cold crystallization event in quenched CPU results in lower overall crystallinity. In terms of

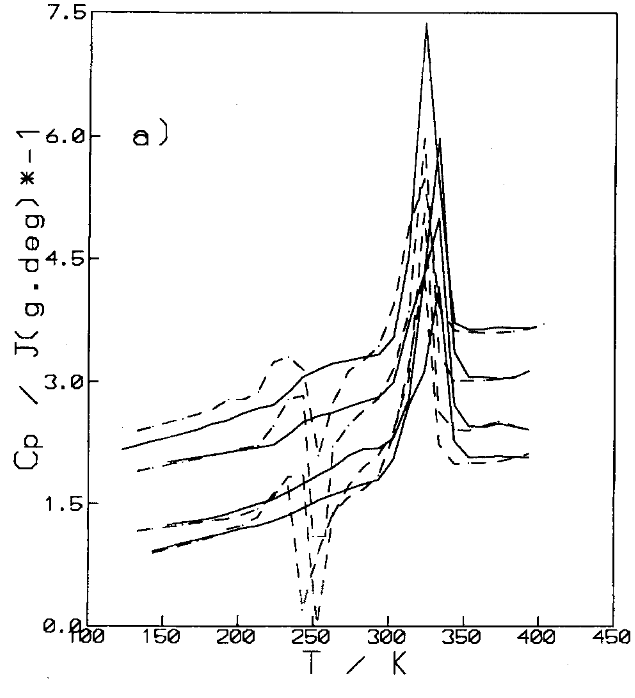

FIGURE 1 Specific heat capacities of initial (solid lines) and quenched (broken lines) samples of p-TIPNs of the following CPU (S/AA) compositions (from top to bottom):
a) 100/0; 90/10; 80/20; 65/35.
b) 35/65; 20/80; 10/90; 0/100.
Beginning from the second curve from the bottom, each successive curve was shifted upwards by 0.5 J/g.deg.

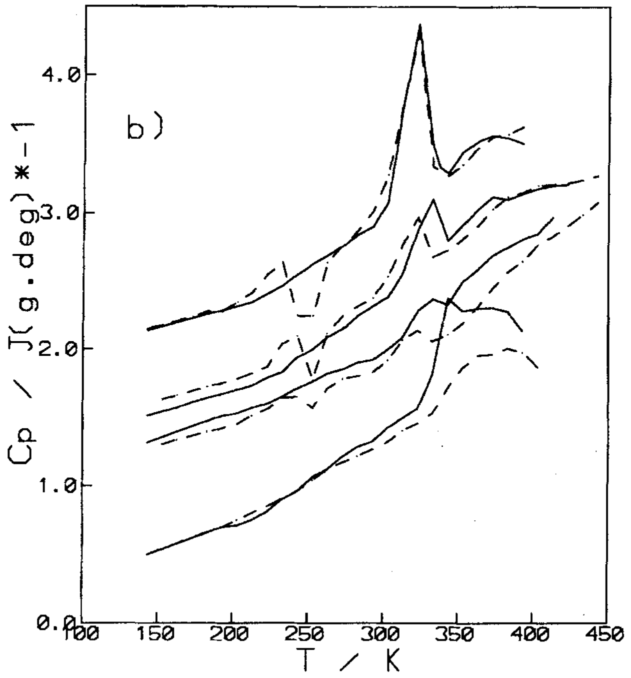

FIGURE 1 (Continued).

the modified Thompson equation [9],

$$T_m = T_m^0\,[1 - \mathrm{const}/\langle D\rangle] \tag{1}$$

(where T_m^0 is the melting point of an ideal, "infinitely long" crystal), the concomitant depression of the melting point, T_m, in the quenched sample should be attributed to formation of less stable microcrystals of smaller size $\langle D\rangle$.

As typical for a non-crystallizable polymer, one observed only Δc_{p2} jumps in the glass transition intervals of both initial and quenched samples of S/AA (Fig. 1b); the shift of T_{g2} to higher temperatures concomitant with the decrease of the corresponding Δc_{p2} for the latter sample, most probably, is due to the high temperature post-polymerization during the first heating run.

Judging by the occurrence of melting endotherms on thermograms of both first and second heating runs, BAG retains crystallizability in p-TIPNs in nearly the whole range of its compositions (Figs. 1a and 1b). As could be inferred from Eq. (1), a nearly composition-invariant T_m in both initial and quenched samples (330 ± 3 K and 325 ± 3 K, respectively) implies that the mean size of BAG microcrystals in p-TIPNs was also essentially independent of composition. It is pertinent to remark here that linear extrapolation of the melting heats of BAG microcrystals, ΔH_m (calculated per unit mass of p-TIPN), yields $\Delta H_m = 0$ not at CPU content $W = 0$ as would be consistent with the assumption of a sharp interface between pure microphases of BAG and S/AA, but rather at $W = 0.1$ (Fig. 2). This result implies the hindrance to crystallizability of BAG in p-TIPNs (presumably, due to existence of small but finite miscibility between BAG and S/AA).

A similar conclusion results from the analysis of composition dependencies of T_g and corresponding Δc_p of p-TIPNs (Figs. 3, 4). As can be seen from Figure 3, dependencies of Δc_p for both initial and quenched samples of p-TIPNs on CPU content are reasonably linear, both intersecting the non-zero value on the ordinate ($\Delta c_p = 0.05$ J/g.deg) at $W = 0$. Moreover,

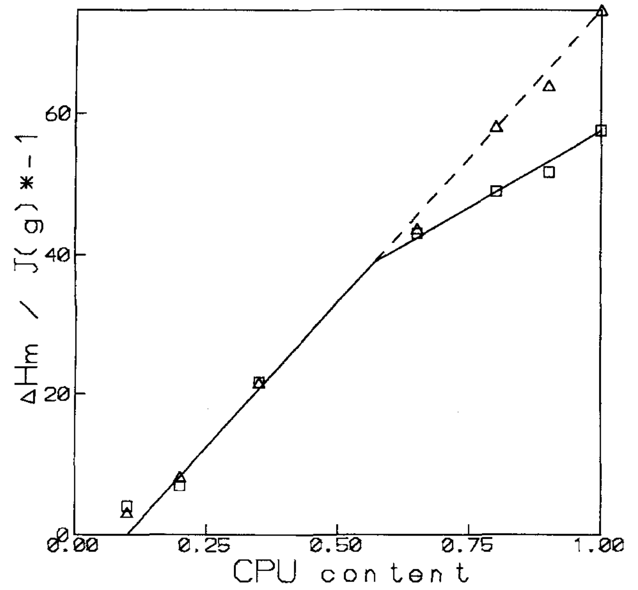

FIGURE 2 Composition dependence of BAG melting heats) calculated per unit mass of p-TIPNs) for initial (triangles) and quenched (squares) samples.

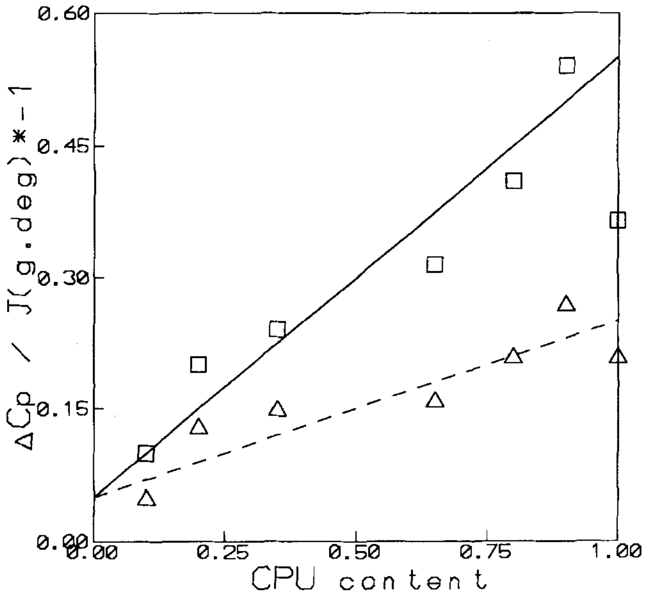

FIGURE 3 Composition dependence of Δc_p jumps for initial (triangles) and quenched (squares) samples of p-TIPNs.

values of T_g for both initial and quenched samples of p-TIPNs are roughly composition-invariant, the corresponding average values (solid and broken lines, respectively) being some 5–7°K higher than the T_{g1} of CPU (Fig. 4). Both these sets of data can be reasonably accounted for by Couchman's equation for miscible polymer blends [10],

$$\ln T_g = [\ln T_{g1} (1 - W) + \ln T_{g2} W] K / [(1 - W) + WK] \qquad (2)$$

(where $K = \Delta c_{p2} / \Delta c_{p1}$) assuming composition of the mixed microphase to be, roughly, CPU (S/AA) $\cong$ 90/10.

If follows from the above results that the as-quenched samples of p-TIPNs of whatever nominal composition consist of a mixed microphase of fixed composition [CPU/(S/AA) = 90/10] and of an essentially pure microphase of the excess of S/AA. At high CPU contents, the glass transition of this latter microphase could not be detected on heating thermograms due to its fortuitous overlap with the BAG

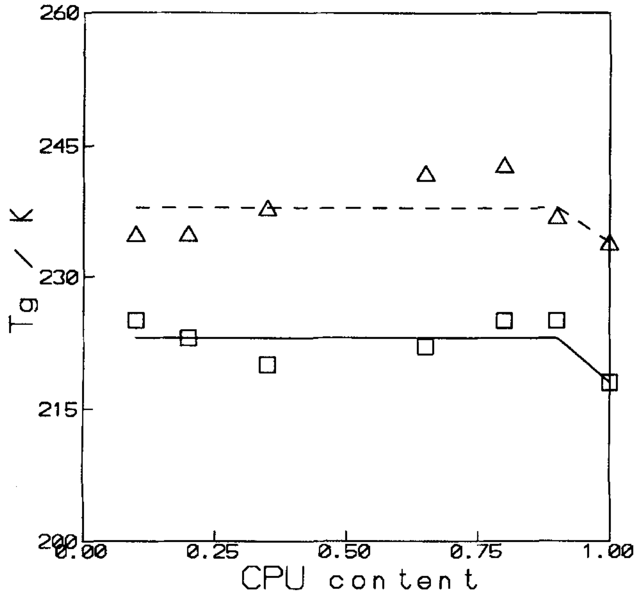

FIGURE 4 Composition dependence of T_g for initial (triangles) and quenched (squares) samples of p-TIPNs.

melting endotherm (Fig. 1a); however, at low CPU contents the expected Δc_p jumps at the T_{g2} of pure S/AA microphase were clearly observed slightly above BAG melting interval (Fig. 1b).

More complex phase morphology (*i.e.*, coexistence of essentially pure microphases of crystallized BAG and S/AA, and of the mixed CPU/(S/AA) microphase) should be expected in the initial samples of p-TIPNs. In these samples, the amount of pure S/AA microphase will change due to crystallization of BAG in CPU; thus, the observed elevation of T_g (compared with quenched samples) can be a result of constraints on segmental mobility of non-crystallized material by BAG microcrystals, and/or of enrichment of the mixed CPU/(S/AA) microphase with S/AA.

X-ray Scattering

The WAXS pattern of pure CPU (Fig. 5) is typical for a semi-crystalline polymer (that is, occurrence of several sharp diffraction peaks

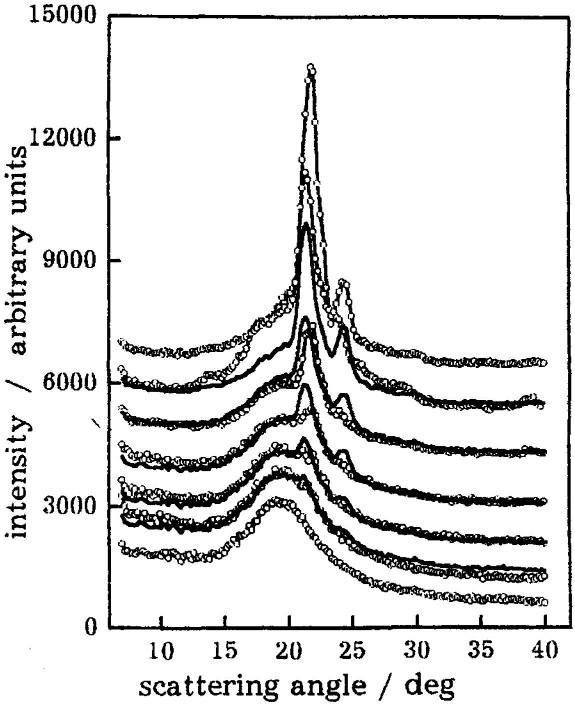

FIGURE 5 Experimental (points) and additive (solid lines) WAXS curves for p-TIPNs of the following CPU/(S/AA) compositions (from top to bottom: 100/0; 90/10; 80/20; 65/35; 20/80; 10/90; 0/100. Beginning from the second curve from the bottom, each successive curve was shifted upwards by 5 digits.

superposed on a broad amorphous halo). As could be expected, the angular positions of cited diffraction peaks (at $2\Theta = 17.6, 21.2$ and 24.2 deg., respectively), as well as X-ray crystallinity ($\langle X \rangle = 0.50$) and the mean size of microcrystals ($\langle D \rangle = 6.9$ nm) derived from WAXS data for CPU, rather closely matched those of an individual semicrystalline BAG-2000 [8]. Thus, the diffraction maximum at $2\Theta = 25$ min on the SAXS curve of pure CPU (Fig. 6) can be safely atrributed to microcrystallites of BAG, the centers of which are separated, on the average, by a distance $\langle L \rangle = 21$ nm.

Both the low overall intensity and the smooth shape of the SAXS curve for pure S/AA (Fig. 6) can be regarded as the experimental evidence for absence of large-scale structural heterogeneities. The diffuse maximum around $2\Theta = 19.2$ deg on the WAXS curve of this

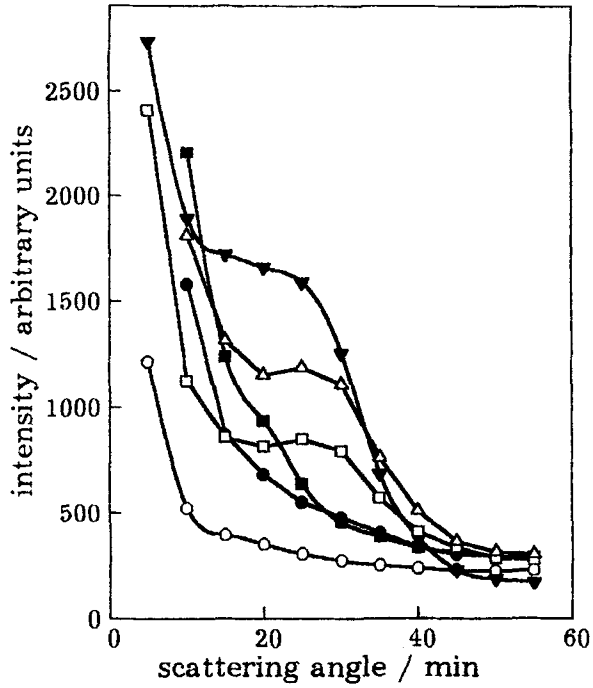

FIGURE 6 SAXS curves for p-TINPs of the following CPU/(S/AA) compositions (from top to bottom): 100/0; 90/10; 80/20; 65/35; 20/80; 10/90; 0/100.

sample (Fig. 5), most likely, is caused by intramolecular effects (*e.g.*, local spatial correlations between phenyl rings of styrene sequences [7]).

The experimental WAXS curves for all p-TIPNs, approximately, match corresponding additive curves (solid lines in Fig. 5). This means that both crystallizability of BAG in CPU, as well as the mean sizes of BAG microcrystallites are rather little affected by S/AA. A similar conclusion applies to SAXS data (Fig. 6): as could be expected, the overall SAXS intensity increases with CPU content, whereas the angular position of the SAXS maximum (that is, the long period) remains almost unchanged. Thus, the arguments about weak (although non-negligible) affinity between CPU and S/AA, as derived from calorimetry, are qualitatively consistent with X-ray scattering data.

CONCLUSIONS

1. Crystallizability of BAG is the main cause of microphase-separated morphology of CPU.
2. Limited miscibility of CPU with S/AA significantly affects the phase morphology of p-TIPNs on their base. Mixed microphase of fixed composition [CPU/(S/AA) = 90/10] and essentially pure microphase of S/AA are the main structural entities in as-quenched samples of p-TIPNs of whatever nominal composition. More complex phase morphology (that is, coexistence of essentially pure microphases of crystallized BAG and of S/AA, and of the mixed CPU/(S/AA) microphase enriched with S/AA) is expected for initial samples.

Acknowledgements

This work was supported by the INTAS project 93-3379-ext, by the NATO Research Fellowship grant for E.G.P., and by the NATO Expert Visit grant HTECH.EV 960944 for V.P.P. Constructive criticism of the reviewers of the original manuscript is also gratefully acknowledged.

References

[1] Lipatov, Yu. S. and Sergeeva, L. M., *Interpenetrating Polymer Networks* (Naukova Dumka, Kyiv, 1979) (in Russian).

[2] Sperling, L. H., *Interpenerating Polymer Networks and Related Materials* (Plenum Press, New York, 1981).

[3] Sergeeva, L. M., Grigoryeva, O. P. and Brovko, A. A., *et al.*, *Zhurn. Prikl. Khim.* No.6 (1977).

[4] *Manual on Chemistry and Physics of Polymers*, Kurenkov, V. F., Ed. (Khimia, Moscow, 1990) (in Russian).

[5] Privalko, V. P. and Titov, G. V., *Vysokomol. Soed., Ser. A.* **21**, 348 (1979).

[6] Kitaigorodsky, A. I., *X-ray Structural Analysis of Microcrystalline and Amorphous Substances* (Gostekhizdat, Moscow, 1952) (in Russian).

[7] Lipatov, Yu. S., Shilov, V. V., Gomza, Yu. P. and Kruglyak, N. E., *Characterization of Polymer Systems by X-ray Scattering Methods* (Naukova Dumka, Kyiv, 1982) (in Russian).

[8] Yagfarov, M. Sh., Vlasov, V. V. and Yagfarova, T. A., in *Structure and Mechanical Properties of Polymers* (Naukova Dumka, Kyiv, 1976), p. 18 (in Russian).

[9] Mandelkern, L., *Crystallization of Polymers* (McGraw-Hill Book Co., New York, 1964).

[10] Couchman, P., *Macromolecules* **13**, 1272 (1980).