Nano-Organization and Polymers Viscous Flow

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Opinion

It is generally believed that the mechanism of viscous flow of polymers on movement of chains relative to each other due to the movement of segments. However, nana-organization polymer is formed during synthesis of polymers, and it has a thermodynamic nature. The structure of the nana-organization includes the different content and size of the ordered formations, their possible location in the polymer volume, the packing density of the passing chains in the disordered part, which determines the degree of its ordering [1-3]. The temperature dependence of the viscosity of the homologues of atactic polystyrene in the coordinate equation of Arrhenius detect an abrupt change in the region of 125-130, and 145-150 °C ($M\eta=4.10^4$) (PS-1), 165-170 and 200-205 °C ($M\eta =2.2.10^5$) (PS-2) and 185-190 °C ($M\eta=8\times10^5$) (PS-3). These changes are explained by the manifestation of ρ_0- and ρ_1-phase transitions in PS-1, ρ_1- and ρ_2- in PS-2 and ρ_2-transition in PS-3. The activation energy of the viscous flow of PS-1 decreased from 64 to 50 and to 46kJ/mol, respectively, and from 65 to 40kJ/mol with the manifestation of the ρ_1-transition in PS-2, and from 140 to 40kJ/mol in the case of PS-3. About the existence of change in the structure of the nana-organization of these homologues is evidenced by the wide angle X-ray diffraction data obtained by heating them.

Phase transitions also determine the complex temperature dependences of the dynamic viscosity of cis-1.4-polyisoprene (97% cis-1,4-units, $M\eta=9.8\times10^5$, T_c-69 °C) (PI) and cis-1.4-polybutadiene (98.5% cis-1,4-units, $M\eta=3\times105$, T_c-105 °C) (PB), butyl rubber ($M\eta=3\times10^5$, T_c-73 °C) (BR), polyisobutylene ($M\eta=1.1\times10^6$ and $M\eta= 7.5\times10^4$, T_c-73 °C) (PIB-1, PIB-2, respectively) (Figure 1a). The cohesion energy of all polymers is approximately the same, with the exception of PB. A sharp decrease in the activation energy of the viscous flow of PB and PI is due to the complete disintegration of their nana-organization at 90 °C and 118 °C, respectively according to the data of the diffusion method (ρ_d-transition) (Figure 1b). The use of diphenyl guanidine as a penetrant, which is not indifferent to the structure of the PI nana-organization (caused a decrease in its viscosity), accompanied by ρ_d-transition till 118 °C in case of PI (Figure 1b). The manifestation of the ρ_4-phase transition in PI, the ρ_6-transition in PB at 65 °C, and especially the ρ_6-transitions in PIB at 120 °C cause increase size and decrease content of nanostructures and increase of volume content in disorder part of polymer. The temperature of phase transitions is related to the T_c of polymers by the ratio regardless of their chemical structure: $T_i = \{[1.2+0.2\ (i-2)]\pm0.05T_c$, where i is the ordinal number of the phase transition [1]. The decrease in polymer viscosity with an increase in temperature is explained by an increase in the size of nanostructures while at the same time increasing the free volume in the disordered part of the nana-organization. Accordingly, the high viscosity of polymers is a manifestation not so much of the structural characteristics of macromolecules as of the degree of ordering of the nana-organization. This is most clearly manifested with a slight deformation (slight stress). The complex temperature dependence degenerates with

increasing deformation. The activation energy of the viscous flow of PB decreased from 12.08 to 1.52kJ/mol, from 11.84 to 1.98kJ/mol for PI, from 44.57 to 0.43kJ/mol for PIB, as well as from 8.9 to 1.97kJ/mol in BR. The activation energy of the viscous flow of polymers above the temperature of the ρ_d-phase transition indicates that their flow in this case is a consequence of the movement of

segments. In other words, the activation energy of flow above ρ_d-phase transition does not depend on the temperature. Based on this, to observe the transition from state with the non-Newtonian flow to the Newtonian state of the polymer higher of the temperature ρ_d-phase transition.
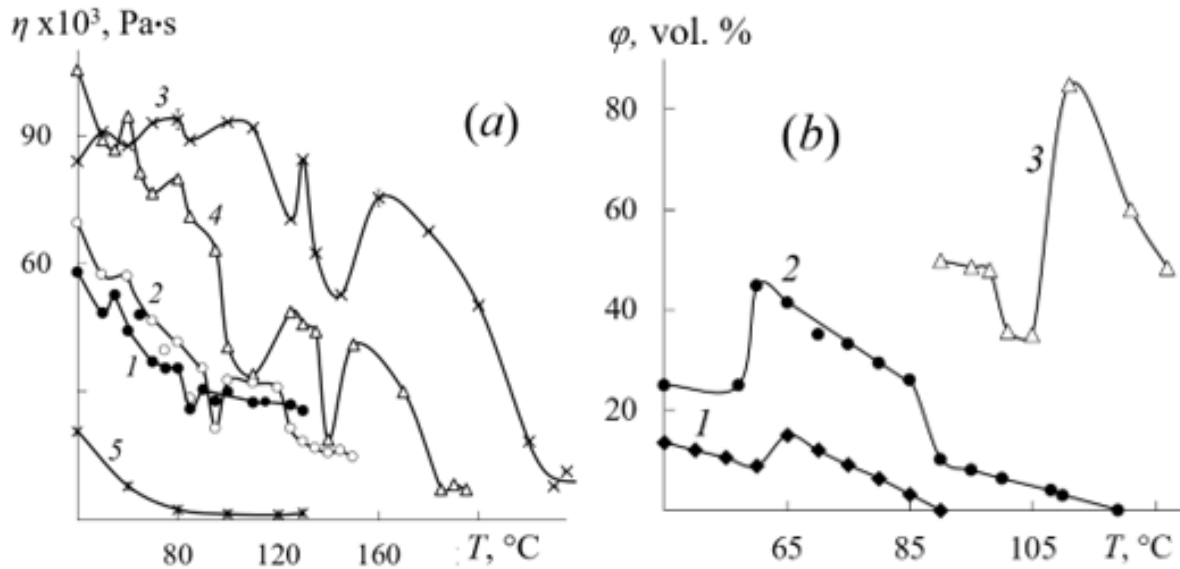

Figure 1: Temperature dependences of the dynamic viscosity of PB (1), PI (2), PIB-1 (3), PIB-2 (5) and BR (4) (a) and the volume content of nanostructures in them (b).

References

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