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# TWO KINDS OF NANOSCALE DYNAMIC HETEROGENEITY IN SINGLE-PHASE POLYMER BLENDS AND THEIR COMMON ORIGIN

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Abstract: Differential scanning calorimetry (DSC) and laser-interferometric creep rate spectroscopy (CRS) were used for kinetic and discrete analysis of segmental motion within (and close to) glass transition range in polystyrene – poly($\alpha$-methyl styrene) (PS/PMS) and polystyrene – poly(vinyl methyl ether) (PS/PVME) miscible blends. Two kinds of segmental dynamics heterogeneity were found. Separate 'unfreezing' of PS and PMS segmental motions was observed that manifested itself in two $T_g$s and simultaneous large drop in the Tg s, as well as glass transition activation energy, motional event scale and cooperativity degree values, down to the $\beta$-relaxation parameters. The wide activation energy dispersion within a single broad glass transition in PS/PVME blends was found, and this relaxation region was subdivided, by CRS, into several predicted kinds of segmental motion. Both results are treated in the framework of the concept of common segmental nature of $\alpha$- and $\beta$- relaxations in flexible chain polymers.

## INTRODUCTION

Glass transition characteristics in miscible polymer blends may manifest a special behavior differing considerably from those in pure polymers. Thus, an extraordinary broad glass transition range, $\Delta T_g$, or pronounced deviations from the rule of mixtures, or an asymmetry of segmental relaxation dispersion have been observed (Refs.1-6). To account for these 'anomalies', a few models have been proposed (Refs.7-9) in which the heterogeneity of segmental dynamics within $\Delta T_g$ range has been assumed. However, up to recently understanding of this phenomenon still remained incomplete for lack of direct experimental data. We suppose our combined DSC/CRS study (Ref.6 and this communication) fills up this gap to some extent.

## EXPERIMENTAL

Atactic PS ($M_w \approx 10^5$, $M_w/M_n = 1.06$), PMS ($M_w = 2\cdot 10^5$, $M_w/M_n = 2.0$) and PVME

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($\overline{M}_w$ = $4\cdot10^4$, $\overline{M}_w/\overline{M}_n$ = 2.3) were used for preparing of the series of PS/PMS and PS/PVME blends under conditions providing their miscibility and solvent removing (Ref. 6). Blend miscibilty was proved by mid- and far-IR spectroscopy data obtained for PS/PMS blends
(Ref. 10) and in NMR measurements of PS/PVME blends (Ref. 11). DSC measurements (Perkin-Elmer DSC-2, 200-470 K, 5-40 K $min^{-1}$) allowed us to determine, as earlier (Ref. 12), the temperatures, $T_g$ and $\Delta T_g$; heat capacity, $C_p$; activation energy, Q, dispersion; motional event scale [Donth's parameter, $V_{coop}$ (Ref. 13)], and the degree of intermolecular cooperativity, $Z = V_{coop}/V_s \approx Q_\alpha/Q_\beta$, of segmental motion within the glass transition. Here, $V_s$ is the statistical Kuhn segment volume, and $Q_\alpha$ and $Q_\beta$ are the activation energies of α- and β-relaxations. Original CRS technique using a laser interferometer for measuring of creep rates at small tensile stress and different temperatures, on the basis of deformation increment of
$10^{-2}$- $10^{-1}$ %, was utilized; it has been described in detail elsewhere (Refs.14-16). Of importance, CRS is superior in resolution to generally used relaxation spectrometry techniques and allows the discrete analysis of segmental motions constituting a broad relaxation transition region.

## RESULTS AND DISCUSSION

The first kind of dynamic heterogeneity found consisted in manifestation of two rather narrow glass transitions and quasi-independent dynamic behavior of PS and PMS segments in their miscible blends (Ref.6). Fig.1 shows the obtained dependencies of glass transitions' parameters, $T_g$, Q and Z, on blend composition. One can see that the $T_g$ values do not change smoothly with composition , they are much displaced downwards in respect to those for pure polymers. The lower $T_g$s are close to the temperatures of β-relaxation, $T_\beta$. Besides, two- or three-fold decrease in the Q values, down to $Q \approx Q_\beta$, is observed, and cooperativity parameter Z dropped from 3-4 in pure polymers down to ~1 in the blends.
Simultaneous drop in $T_g$, Q and Z values gave a coherent idea of why the glass transition exhibits a peculiar behavior in these blends. This result could be interpreted proceeding from the common, Kuhn segmental, origin of intermolecularly coopertive α-relaxation and non-cooperative, Arrhenius β-relaxation in flexible chain polymers (Refs.12, 17, 18). In accord with the IR spectra and heat capacity data (Refs. 6, 10), molecular mixing of PS and PMS chains resulted in loosened segmental packing and excess free volume. It brought about a partial or total collapse of intermolecular cooperativity of segmental motion, i.e. a cardinal decreasing of parameter Z. It means that separate 'unfreezing' of PS and PMS segmental motions, via non-cooperative β-relaxation mechanism, predominated in blend glass transitions. Hence it follows that two $T_g$ s cannot be considered as unconditional evidence of microphase separation in blends; the latter is the point only if the transition parameters coincide with or are close by

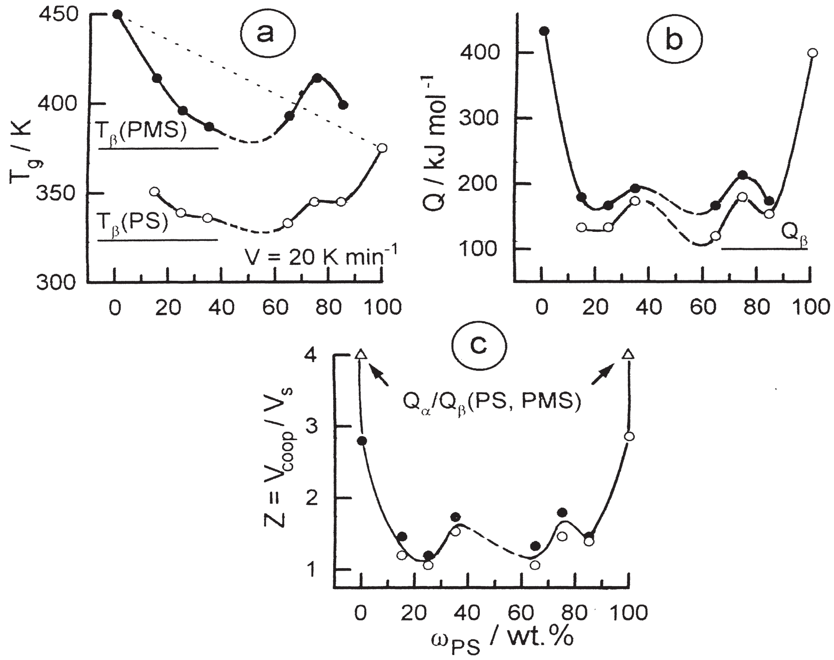

Fig.1: PS/PMS miscible blends: (a) glass transition temperatures, (b) activation energies, and (c) cooperativity degrees of segmental motion in the doublet glass transition as a function of PS content (open and solid circles correspond to PS and PMS components, respectively).

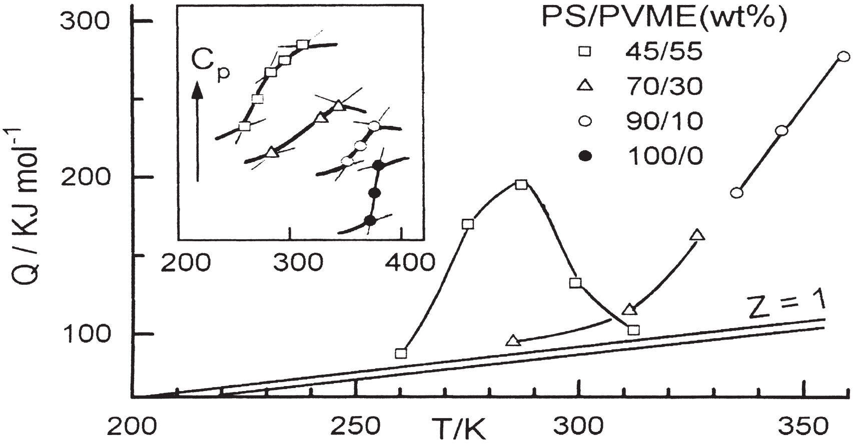

Fig.2: DSC curves (insert, V = 20 K min\+(-1)) and activation energy dispersions for segmental motion in the glass transition of the miscible PS/PVME blends. The band Z = 1 corresponds to Arrhenius Q vs. T relation at $10^{-2}$ Hz.

magnitude to those in pure polymers. It is appropriate to mention that the separate segmental dynamics of both components in single-phase polymer blends has also been observed in NMR experiments (Refs.19, 20).

For miscible PS/PVME blends, the heterogeneity of segmental dynamics in the glass transition manifested itself in quite different way. The only broad, up to 60 K, transition, with two-stage heat capacity step at mid -PS content in a blend, was observed on the DSC curves (see the insert in Fig.2). The latter allowed to estimate the activation energies by displacement with heating rate of five characteristic temperatures within $\Delta T_g$ range. Fig.2 shows the Q vs.T dependencies obtained over this range for three PS/PVME blends.The wide Q dispersions of different type are seen where the experimental points deviate to different extent from the Arrhenius Q vs.T line. On the whole, cooperativity parameter Z changed from 1, when $Q \approx Q_\beta(PS) \approx 100$ kJ mol$^{-1}$, up to 3 when $Q \approx 300$ kJ mol$^{-1}$.

We assumed that the wide Q dispersions were caused , again, by some breakdown of motional cooperativity and probable manifestation, simultaneously, of cooperative and low-cooperative or non-cooperative motions within the glass transition. Besides, PVME as polymeric plasticizer may, presumably, play the subordinated role in this case. Proceeding from the common nature of α- and β-relaxations and the DSC data (Refs.6, 12), one could assume *a priori* manifestation of up to eight kinds of Kuhn segment motions within or below $\Delta T_g$ range in miscible PS/PVME blends (Table 1).

Fig.3 shows the creep rate spectra obtained for three blends, under extension and the indicated experimental conditions, over the temperature region of Kuhn segmental motion, i.e. from $T_\beta$(PVME) to $T_g$(PS). The $\Delta T_g$ range is marked here by the bold lines. As it was expected, CRS permitted, really, to subdivide this broad region into multiple constituent relaxations (creep rate peaks). The spectra respond discretely to arising of an each kind of segmental motion. Significantly, their comparing with the expectations of Table 1 testifies to validity of our approach since the peaks 1-7 correspond, by their temperature location, to predictions. The spectral contours are different and depend on blend composition. As it follows from Figs.2,3 and the right columns in Table 1, only peaks 5, 6 and 7 correspond to $\Delta T_g$ ranges estimated by DSC. Cooperative and low-cooperative motion of dissimilar segments (Z = 2-4, peaks 5), or non-cooperative and low-cooperative motion of PS segments (peaks 6 and 7) basically constitute a broad $\Delta T_g$ range in 45/55, 70/30 and 90/10 blend compositions, respectively. At the same time, there is no indications to α-relaxation in PS component while the faint peaks 1-3, which have to be assigned to PVME nanodomains, could be discerned in the spectra.; their relative contribution enhances with increasing of PVME fraction in a blend.

Nanoscale dynamics (of ca.2 nm size Kuhn segments) is discussed virtually herein, therefore, the spectra obtained indicate incomplete nanoscale level mixing in PS/PVME single-phase

Table 1. Predicted kinds of possible segmental motions within or below the glass transition in PS/PVME miscible blends and their manifestation in the creep rate spectra

| Motional event | Cooperativity degree Z | Expected T(K) at $10^{-2}$ Hz | Creep rate peaks at PS/PVME ratio | | |
|---|---|---|---|---|---|
| | | | 45/55 | 70/30 | 90/10 |
| 1. PVME, β-relaxation | 1 | 170 – 190 | + | + | - |
| 2. PVME, intermediate relaxation | 2 | 200 – 220 | + | + | - |
| 3. PVME, α-relaxation | 3 | 240 – 250 | + | - | - |
| 4. PS, β-relaxation when contacting with PVME chains | 1 | 260 – 270 | + | - | - |
| 5. 1 PS + (1÷3) PVME segments cooperation | 2÷4 | 270 – 290 | + | + | + |
| 6. PS, β-relaxation | 1 | 300 – 320 | - | + | + |
| 7. PS, intermediate relaxations | 2÷3 | 330 – 360 | - | + | + |
| 8. PS, α-relaxation | 4 | 370 – 380 | - | - | - |

Note: the signs +, + or + indicate a presence of the slight, medium or basic peaks in the spectra, respectively.

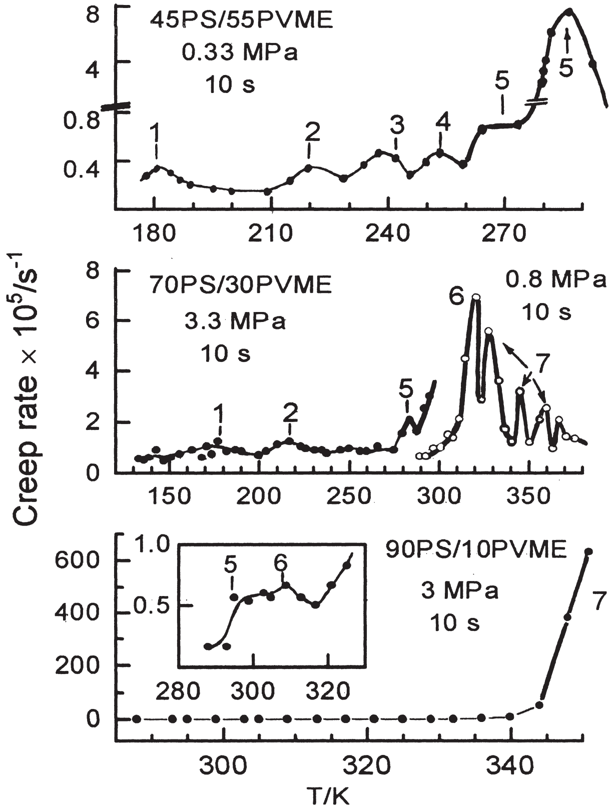

Fig. 3. PS/PVME creep rate spectra. Bold lines correspond to the glass transition range.

blends. It should be noted that the CRS possibilities for semi-quantitative probing of nanoscale compositional heterogeneity were recently shown for interpenetrating networks (Ref.16).

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