

The Supermolecular Structure of Poly(vinyl Chloride)–Poly(methyl Methacrylate) Blends

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Synopsis

Investigations of the supermolecular structure of PVC/PMMA blends, covering a wide range of composition, are presented. It was found that a transition layer exists between PVC and PMMA phases. The thickness of the transition layer is independent of blend composition. The scattering intensity distribution function for blends is characteristic of isotropic, amorphous systems with a completely random distribution of phases. It was shown that scattering intensity distribution function may be used for calculation of a distribution, which corresponds a two-phase system with sharp phase boundaries. Values of correlation lengths, inhomogeneity lengths, and specific surfaces were then calculated. A model of the supermolecular structure of PVC/PMMA blend was finally proposed.

INTRODUCTION

Physical properties of polymer blends are mostly dependent on their supermolecular structure. The determination of this structure is realized by means of various methods, including small angle x-ray scattering (SAXS), which is frequently used. The SAXS method is particularly suitable for investigations of objects of colloidal dimensions and, therefore, is very useful for studies of the structural constituents of polymers. An important aspect of this study is determination of the thickness of the transition layer between phases with differential electron density. Vonk and Pijpers¹ and Ruland² determined the thickness of the transition layer between crystalline and amorphous phases of semicrystalline polymers. Koberstein and Stein³ estimated the diffuse phase boundary thickness of two segmented polyurethane block copolymers. The determination of transition layer thickness and other parameters of the supermolecular structure is of great importance since they affect the physical properties of polymers.

Thanks to modern instrumentation, i.e., position sensitive counters, high power x-ray tubes, computers, etc., and to the employment of new theoretical achievements in the analysis of scattering curves, one can determine, more and more precisely, many parameters of the supermolecular structure of multiphase polymer systems.⁴

Two-phase systems with sharp phase boundaries may be characterized by a correlation length and average inhomogeneity lengths.⁵ The correlation length (Porod refers to it as to the reduced inhomogeneity length) may be calculated

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from the SAXS pattern. SAXS intensity distribution is dependent on fluctuations of electron density in the volume of the sample. The distribution is given by

$$I(s) = V \cdot \int_0^\infty 2r^2 \cdot \gamma(r) \frac{\sin 2\pi sr}{sr} dr, \quad s = \frac{2 \sin \vartheta}{\lambda} \quad (1)$$

where $\gamma(r)$ is the correlation function, ϑ is the angle of scattering, λ is the wavelength, and V is the illuminated sample volume. For a completely random distribution of two phases, Debye and Bueche⁶ has shown that

$$\gamma(r) = \exp(-r/l_p) \quad (2)$$

where l_p is correlation length. In this case, eq. (1) has the following solution:

$$I(s) = \frac{A}{(1 + 4\pi^2 \cdot s^2 \cdot l_p^2)^2} \quad (3)$$

where A is a constant.

Equation (3) can be expressed as

$$[I(s)]^{-1/2} = A^{1/2}(1 + 4\pi^2 s^2 l_p^2) \quad (4)$$

A plot of $[I(s)]^{-1/2}$ vs. s^2 is thus linear and l_p may be derived from the slope.

After some modifications, the method described above may be used for systems with a transition layer between phases with different electron densities. In this paper, we employ a modified method for the characterization of the supermolecular structure of PVC/PMMA blends of various compositions. The supermolecular structure of the blends investigated is characterized by the following parameters: the thickness of the transition layer E , the correlation length, the average inhomogeneity lengths, and the specific surface S/V .

EXPERIMENTAL

Films were prepared from PVC/PMMA blends with compositions covering a wide range (90:10, ..., 10:90 PVC/PMMA). The blends were obtained by mixing of the components of a Brabender vibrator. Films of thickness 0.2 mm were formed by rolling of the blends at 170°C during 1 h at a pressure of 2×10^7 Pa.

SAXS measurements were performed using a Rigaku-Denki diffractometer with x-ray tube (2 kW) employing a copper target. CuK_α radiation ($\lambda = 1.54 \text{ \AA}$) was monochromatized by means of a Ni-filter with 0.015 mm in thickness and by a pulse height analyzer connected with a scintillation counter.

The X-ray beam, emitted by a linear focus of the tube, was collimated by three slits located between the tube and the sample. The distance between the sample and the detector was 350 mm.

A vacuum path eliminating air scattering was installed between the counter and the sample. The path was connected with a vacuum pump. SAXS

patterns were taken in the range 0.09 – 5.5° using step scanning, a fixed count mode with a step of 0.02° in the range 0.09 – 2.75° and of 0.05° in the range 2.75 – 5.5° . The time of counting was 100 s.

The X-ray tube was operated at 40 kV and 35 mA. SAXS patterns were normalized on the basis of transmission coefficients. The coefficient was measured as the ratio I_s/I_0 , where I_s is the transmitted intensity and I_0 is the intensity of the primary beam.

The patterns were desmeared using Vonk's method.⁷

The weight functions of the collimation system were calculated using the method of Hendricks and Schmidt.⁸ Calculations were performed employing an IBM-370 computer and the computer program FFSAXS-5 elaborated by Vonk.

WAXS investigations were carried out on the Rigaku-Denki diffractometer. Thermal investigations were made using a Dupont 990 thermal analyzer. IR spectra of blends were taken with the aid of a Beckman IR 4220 spectrophotometer. Spectra were recorded in the range 400 – 600 cm^{-1} .

RESULTS AND DISCUSSION

IR absorption measurements reveal that all the absorption bands characteristic of pure homopolymers, i.e., PVC and PMMA, are visible on the IR spectra of blends with various compositions. There are no bands indicating the appearance of new chemical bonds.

Thermal properties of polymer systems are dependent on whether a system is single-phase or two-phase. For instance, a mixture of miscible polymers has one glass transition temperature; its value depends on the weight fractions of the components in the mixture.⁹ Polymer systems composed of incompatible polymers have two glass temperatures characteristic of the mixture components.

A thermogram of PVC/PMMA blends is given in Figure 1. The thermogram shows the two glass transition temperatures of the homopolymers; $T_{g\text{PVC}} = 353\text{ K}$ and $T_{g\text{PMMA}} = 378\text{ K}$.

IR and DSC results confirm that PVC/PMMA blends are two-phase mixtures of immiscible components. WAXS patterns of PVC/PMMA exhibit broad, diffuse maxima, indicating that the blends are completely amorphous.

Considering the results of IR, DSC, and WAXS measurements, one can state that the PVC/PMMA blends are a completely amorphous two-phase system. Determination of the supermolecular structure of such a system is possible with the aid of SAXS method.

SAXS patterns do not show any scattering maxima; the intensity decreases continuously with an increase in scattering angle. SAXS patterns of this kind are characteristic of two-phase, isotropic systems with completely random distribution of phases.

The SAXS pattern for PVC/PMMA blend is presented in Figure 2. The pattern exhibits clearly visible background scattering. The background intensity increases with an increase in scattering angle. It was found that the angular dependence of background intensity satisfied the following relation: $y = a + b(2\theta)^n$. Knowing the analytical form of background function, one can subtract the background from the scattering curve.

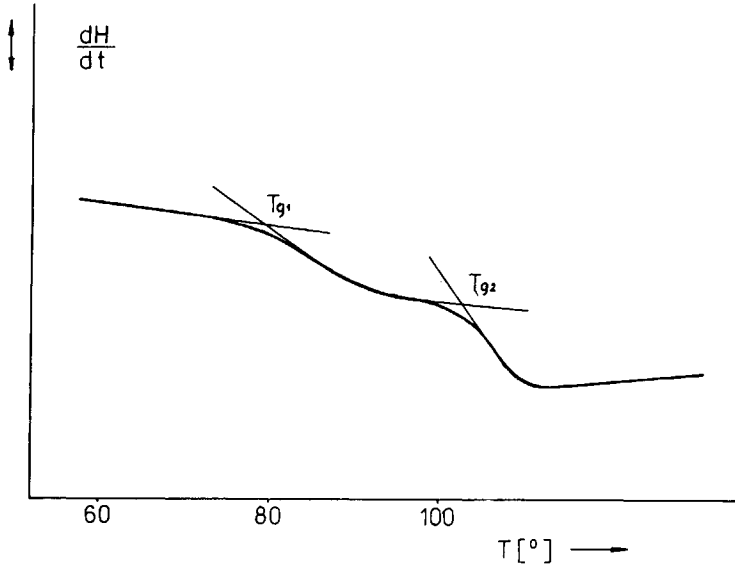


Fig. 1. DSC thermograms of a blend 70% PVC/30% PMMA.

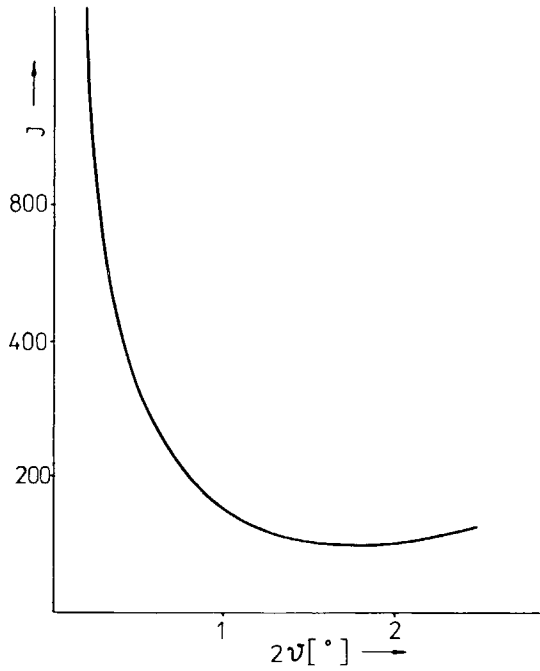


Fig. 2. Relative, smeared SAXS intensity distribution for the blend 90% PVC/10% PMMA.

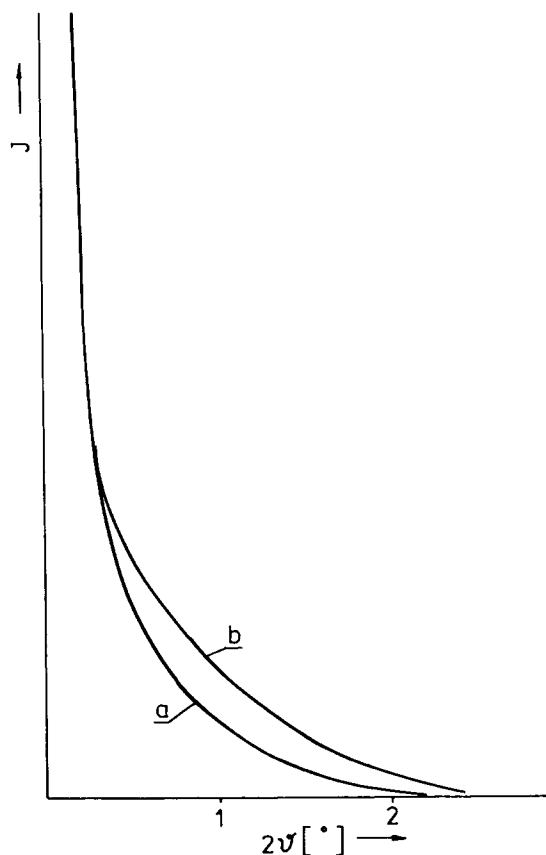


Fig. 3. (a) Relative, desmeared SAXS intensity distribution after subtraction of the background for the blend 90% PVC/10% PMMA; (b) the same curve after correction.

The values of background intensity in the whole range of measurement were calculated and subtracted from scattering curves with the aid of a FFSAXS-5 computer program. The program was also used for desmearing of the SAXS curves.

Desmeared scattering curves are presented in Figure 3 (curve a). For ideal two-phases systems with sharp phase boundaries, Porod's law¹⁰ holds. According to Porod, at large scattering angles, the scattering intensity decreases in proportion to s^{-4} ,

$$\lim_{s \rightarrow \infty} I(s) = k/s^4 \quad (5)$$

where k is Porod's constant.

Aiming at checking whether the Porod law holds in the case of investigated blends, the plot of $I \cdot s^4$ vs. s was made. For systems with sharp phase boundaries, the plot of this kind tends, at large angles, to a straight horizontal line. The curve presented in the Figure 4 decreases continuously after reaching a maximum. This fact indicates that PVC/PMMA blends are a system with a transition layer between phases with different electron densities.

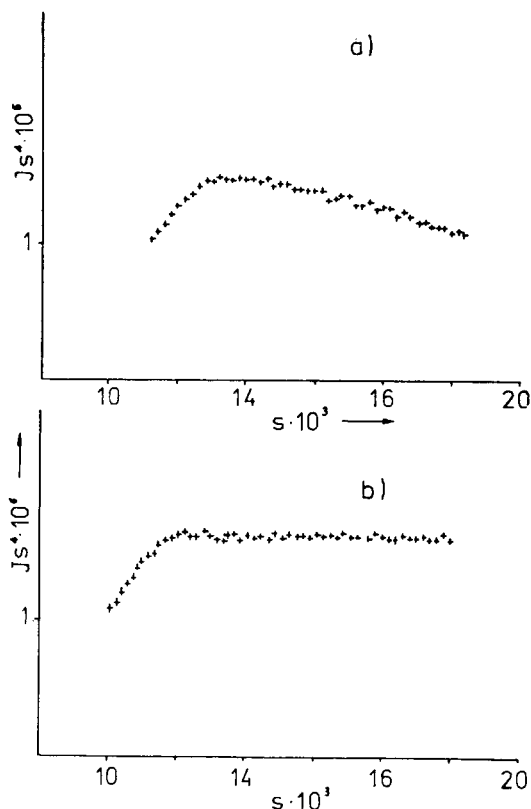


Fig. 4. The plot illustrating the Porod's law: (a) for the blend 90% PVC/10% PMMA; (b) after the correction for the diffuse transition layer between phases.

Aiming at calculation of the thickness of the transition layer, the method of Ruland² was employed. The method is based on the relation

$$\ln I(s) \cdot s^4 = \text{const} - 4\pi^2\sigma^2s^2 \quad (6)$$

A plot of $\ln I(s) \cdot s^4$ vs. s^2 gives a straight line with slope $4\pi^2\sigma^2$. The thickness of the transition layer E is related to the value of σ by

$$E = \sqrt{12} \cdot \sigma \quad (7)$$

The plots used for calculation of E for PVC/PMMA blends with various weight fractions of components are presented in the Figure 5. The calculated values of E are listed in Table I. The scattering intensity for polymer systems with diffuse phase boundaries can be expressed as a product of an intensity due to a system with sharp phase boundaries and a factor arising from diffuseness of the boundaries. The factor is a Fourier transform of a smoothing function, which is related to the shape of electron density variation at the transition layer:

$$I(s) = I_{\text{id}} \cdot H^2(s) \quad (8)$$

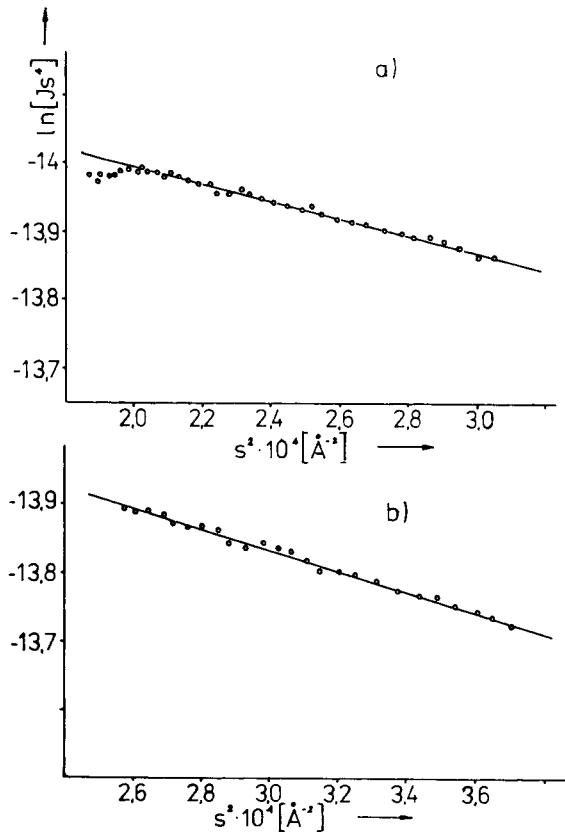


Fig. 5. The plots of $\ln I \cdot s^4$ vs. s^2 for PVC/PMMA blends: (a) 90% PVC; (b) 50% PVC.

For a sigmoidal density variation, the function $H^2(s)$ takes the form

$$H(s) = \exp(-2\pi^2\sigma^2 \cdot s^2) \tag{9}$$

A hypothetical scattering intensity I_{id} , relative to a system with sharp phase boundaries, was calculated using the following relation, resulting from eq. (8):

$$I_{id}(s) = \frac{I(s)}{\exp(-4\pi^2\sigma^2 s^2)} \tag{10}$$

TABLE I
The Values of the Transition Layer Thickness E of PVC/PMMA Blends

E (nm)	Weight fraction of PVC					
	90%	80%	70%	60%	50%	30%
	1.9	2.0	2.1	2.2	2.2	2.1

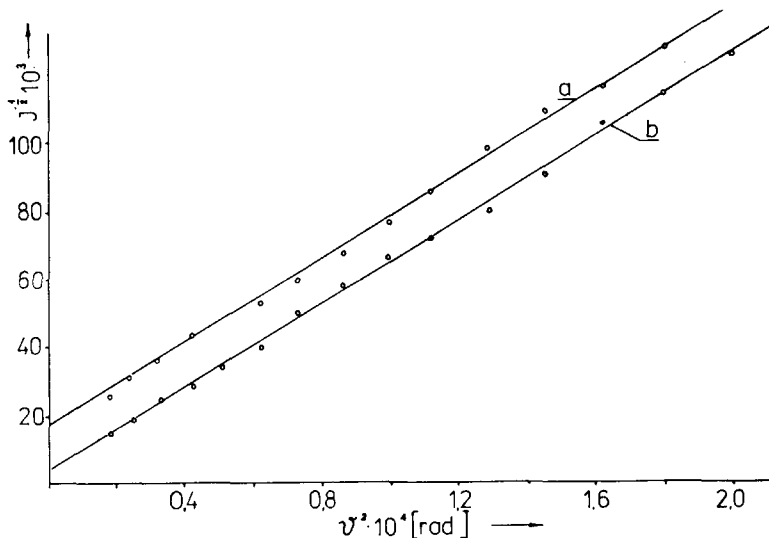


Fig. 6. The plots for calculation of the correlation length l_p : (a) 90% PVC; (b) 70% PVC.

Corrected in this way, scattering intensity distribution is presented in Figure 3(b).

It is clearly visible that the Porod law is fulfilled; at large s , a product $I \cdot s^4$ tends to a constant value [Fig. 4(b)]. This fact confirms that the intensity distribution is related to a system with sharp phase boundaries.

Using the corrected intensity distribution, one can calculate the correlation length by means of eq. (4). Correlation lengths l_p were calculated employing the plots presented in Figure 6. The inhomogeneity lengths, i.e., l_1 (for PVC) and l_2 (for PMMA) were calculated using equations

$$l_1 = \frac{l_p}{1 - \phi_1}, \quad l_2 = \frac{l_p}{\phi_1} \quad (11)$$

The specific surface S/V was determined using the relationship $S/V = 4\phi_1/l_1$, where ϕ_1 is the volume fraction of PVC.

Volume fractions of the phases were found based on the weight fractions and densities of components. The densities of poly(vinyl chloride), $d_1 = 1.38$

TABLE II
The Calculated Values l_p , l_1 , l_2 , and S/V^a

K_1	ϕ_1	l_p (nm)	l_1 (nm)	l_2 (nm)	S/V (m ² /cm ³)
0.9	0.89	4.3	39	4.9	91
0.8	0.775	6.1	27.1	7.9	114
0.7	0.668	7.5	22.6	11.2	118
0.6	0.564	8.2	18.8	14.5	120
0.5	0.463	9.0	16.6	19.4	110

^a K_1 is weight fraction of PVC and ϕ_1 is volume fraction of PVC.

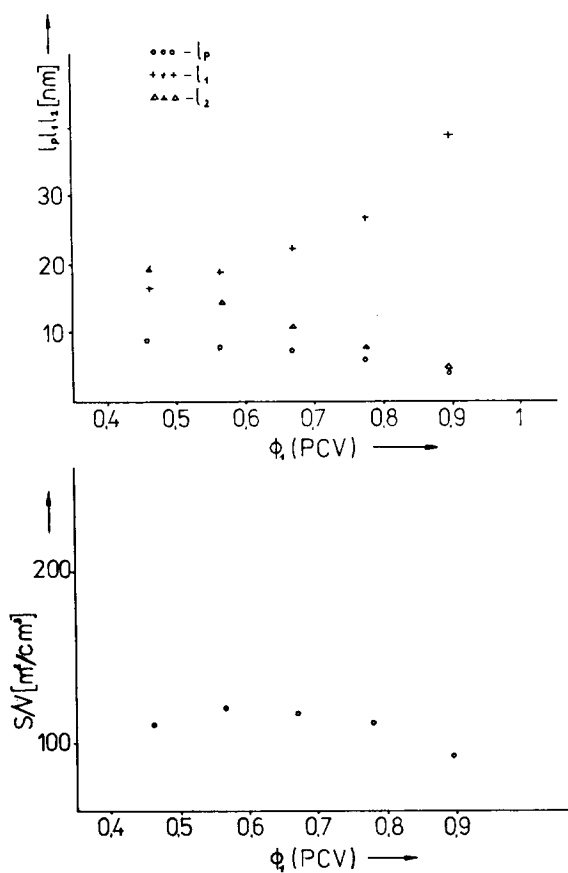


Fig. 7. The plots of l_p , l_1 , l_2 , and S/V vs. the volume fraction of PVC.

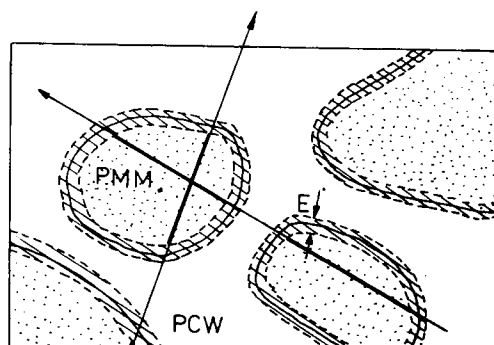


Fig. 8. The schematic diagram of the PVC/PMMA blend. The solid line stands for a quasispecific surface.

g/cm³, and of poly(methyl methacrylate), $d_2 = 1.19$ g/cm³, were determined by means of the pycnometric methods. Calculated values l_1 , l_2 , l_p , and S/V are given in Table II. The plots of l_p , l_1 , l_2 , and S/V vs. the volume fraction of PVC are presented in the Figure 7. The values of l_1 and l_2 give information about the degree of dispersion of PMMA in the matrix formed of PVC.

The length of chords passing through the phase formed of PMMA increases with an increase in its volume, while the mean length of chords passing through the phase formed of PVC decreases. Determined value of a specific surface is related to the surface passing in the middle of a transition layer, and so it should be called a quasispecific surface. Calculated values of the thickness of the transition layer change very slightly with an increase in volume fraction of PMMA. Taking this into account, one can assume that the thickness of the transition layer is independent of the blend composition, but it is dependent on the properties of homopolymers that determine the possibility of diffusion of macromolecules into the transition layer. Considering all the results, a likely model of the supermolecular structure of the PVC/PMMA blends can be proposed. The model is presented in Figure 8.

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