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Inhomogeneous structure of polyurethane networks based on poly(butadiene)diol: 1. The effect of the poly(butadiene)diol content

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The inhomogeneous structure of crosslinked polyurethanes based on poly(butadiene)diol (PBD), 4,4′-diphenylmethane diisocyanate (MDI) and poly(oxypropylene) triol (POPT) prepared with various PBD contents were studied by dynamic mechanical analysis (DMA) and synchrotron small-angle X-ray scattering (SAXS). An inhomogeneous two-phase structure of networks containing PBD was revealed by SAXS. One phase consists of PBD chains while the other of densely crosslinked POPT/MDI network with much higher glass transition temperature. The range of inhomogeneity depends on PBD content, and is estimated as about 70–120 Å from the Bragg spacing. The scattering data are fitted using the Percus–Yevick hard sphere model. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The inhomogeneous two-phase structure in segmented polyurethanes is well-known[1]. One phase consists of soft segments formed by polymer chains with low glass transition temperature, while the other one is constituted of stiff and polar hard segments formed, e.g. by the reaction of diisocyanate with low-molecular-weight diol. The glass transition temperature of the hard segments is much higher than that of soft segments, so that the hard segments act as the physical crosslinks and the soft segments retain rubber elasticity between two glass transition temperatures corresponding to hard and soft segments. The microphase separation is caused by the thermodynamic incompatibility between soft and hard segments due to the big difference in polarity of the components. It results often in the formation of the domains of either of three forms, spheres, cylinders or lamellae, which is determined primarily by the relative volume fractions of the components[1].

Segmented polyurethanes are prepared conventionally by using hydroxy-terminated polyethers or polyesters as a soft segment component[2]. The main factors which determine the structure of the segments are hydrogen bonding, crystallization potential and the glass transition temperature of the components. If (non-polar) polybutadiene is used instead of polyether or polyester, the hydrogen bonding is absent between hard and soft segment phases. Chen-Tsai *et al.*[3] studied the structure and morphology of polyurethanes prepared from poly(butadiene)diol (PBD), toluene diisocyanate (TDI) and 1,4-butanediol (BDO) by SAXS and electron microscopy. They have found that the hard-segment phase is formed by microdomains with sharp interface boundary of the size of a few tens Å when the hard segment content is low. If the hard segment content was increased to 30–70 vol%, the hard-segment phase was found to assume a lamellar morphology. Similar results were obtained by Li *et al.*[4] who used 4,4′-diphenylmethane diisocyanate (MDI) in place of TDI.

The incorporation of chemical crosslinks into inhomogeneous polyurethane structure has a restrictive influence on the size of microdomains, especially if the reaction is performed in a one-stage process. Recently, an inhomogeneous structure of this kind was observed by small-angle X-ray scattering (SAXS) in crosslinked polyurethanes prepared using PBD, MDI and poly(oxypropylene)triol (POPT)[5]. Here it is assumed that one phase consists of non-polar polybutadiene chains, and the other of dense covalent network (formed by the reaction between POPT and MDI). Inhomogeneity has not been detected by d.s.c. in spite of the fact that it has a strong effect on the elastic behaviour of the polymers.

In this work, further investigation was made on the same system where the structure and mechanical behaviour of the inhomogeneous polyurethane networks

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were observed by synchrotron SAXS and dynamic mechanical analysis (DMA) as a function of PBD content.

THEORY

The scattering intensity $I(q)$ from an isotropic material can be expressed in terms of a normalized correlation function (of electron density fluctuation) γ as[6]

$$I(q) \propto \int_0^\infty 4\pi r^2 \gamma(r) \frac{\sin qr}{qr} \mathrm{d}r \tag{1}$$

where $q = (4\pi/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector with λ and θ being wavelength and the scattering angle, respectively. $\gamma(r)$ is defined as the average of the product of two fluctuations in electron density $\Delta\rho(\mathbf{r})$ in two positions $\mathbf{r}_1$ and $\mathbf{r}_2$ at a distance $r = |\mathbf{r}_1 - \mathbf{r}_2|$:

$$\gamma(r) = \frac{\langle \Delta\rho(\mathbf{r}_1)\Delta\rho(\mathbf{r}_2)\rangle}{\langle (\Delta\rho(\mathbf{0})^2)\rangle} \tag{2}$$

Here the average is taken over all directions of the vector $\mathbf{r}_1 - \mathbf{r}_2$.

The correlation function $\gamma(r)$ can be calculated from the scattering intensity profile by the Fourier transform

$$\gamma(r) = \frac{1}{Q}\int_0^\infty q^2 I(q) \frac{\sin qr}{qr} \mathrm{d}q \tag{3}$$

where $Q = \int_0^\infty q^2 I(q)\,\mathrm{d}q$.

A peak in a scattering profile indicates the presence of two-phase structure. The position of the peak ($q_{\max}$) provides an information about the periodic variation in electron density by the Bragg equation[7]:

$$D = \frac{2\pi}{q_{\max}} \tag{4}$$

where D denotes the Bragg spacing. However, a Bragg spacing depends in a complicated way on the arrangement as well as on the structure of all scattering phases. Its direct interpretation depends heavily on the a priori structural model of the system.

The integral Q in equation (3) is independent of the structural details of the system (scattering invariant), and is given in the case of an (ideal) two-phase system with sharp boundaries between phases by[6]

$$Q_{\mathrm{id}} \propto v_1 v_2 (\rho_1 - \rho_2)^2 \tag{5}$$

where v_1, v_2 and ρ_1, ρ_2 are the volume fractions and electron densities of the phases, respectively. Although the proportionality (instrument) constant in equation (5) is not known, for a series of the systems consisting of the same two phases in various proportions, the ratio $Q/(v_1v_2)$ serves as a (relative) measure of the degree of the phase separation[6,8] in such series. That is, the higher ratio $Q/(v_1v_2)$ indicates the higher degree of the phase separation.

The scattering from the two-phase system, formed by microdomains dispersed in a matrix of different electron density, is given by the product of the contributions from the microdomains and the interference term. If the microdomains are approximated as the spheres of a uniform radius R with the 'hard-sphere' interaction, the scattering intensity can be expressed as

$$I(q, R, v) \propto P(q, R) S(q, R, v) \tag{6}$$

where

$$P(q, R) = \left[3\frac{\sin(qR) - qR\cos(qR)}{(qR)^3}\right]^2 \tag{7}$$

is the scattering factor of a sphere, v is the volume fraction of hard spheres and $S(q, R, v)$ is the interference factor.

The exact form of the interference factor is not known but a solution for a low volume fraction of spheres was derived approximately by Fournet[9]

$$S(q, R, v) = \frac{1}{1 + 8v\epsilon\Phi(2qR)} \tag{8}$$

where ϵ is a constant close to unity and $\Phi(2qR) = P^{1/2}(q.2R)$. The further advance has been achieved by Percus and Yevick[10] whose formula for the interference factor reads[10]

$$S(q, R, v) = \frac{1}{1 + 24vG(A, v)/A} \tag{9}$$

where

$$\begin{aligned} A &= 2qR \\ G &= \frac{\alpha}{A^2}(\sin A - A\cos A) \\ &\quad + \frac{\beta}{A^3}(2A\sin A + (2 - A^2)\cos A - 2) \\ &\quad + \frac{\gamma}{A^5}(-A^4\cos A + 4[(3A^2 - 6)\cos A + (A^3 - 6A) \\ &\quad \times \sin A + 6]) \end{aligned}$$

and

$$\alpha = \frac{(1+2v)^2}{(1-v)^4}$$

$$\beta = -\frac{6v(1+v/2)^2}{(1+v)^4}$$

$$\gamma = \frac{v(1+2v)^2}{2(1-v)^4}$$

In practice (see, e.g., ref. 10) it has been found that a better agreement can be achieved to analyse the scattering data from polymer and colloid systems when a hard-sphere interaction radius [R in equations (8) and (9)] is assumed not to be identical with the scattering sphere radius [R in equation (7)]. This difference is interpreted by the existence of a shell around the spheres made by molecules of a polymer or solvent present in the system[9,11]. Therefore, in the following, the hard-sphere interaction radius and sphere radius will be treated as different parameters denoted as R_{HS} and R ($R_{\mathrm{HS}} > R$, cf. *Figure 1*), respectively.

EXPERIMENTAL

Materials

The networks were prepared in the similar way as described in ref. 5. PBD (prepared at the Research Institute for Synthetic Rubber, Kralupy n.Vlt., Czech Republic) used in the synthesis had a number-average molar mass $\overline{M_n} = 5100\,\mathrm{g\,mol^{-1}}$, a narrow polydispersity $\overline{M_w}/\overline{M_n} = 1.1$, a microstructure of 62% vinyl-1,2, 24%

trans-1,4, 14% *cis*-1,4 and a number-average functionality $f_n = 1.91$. POPT (Niax Polyols) has $\overline{M_n} = 710\,\mathrm{g\,mol^{-1}}$ and $f_n = 2.89$. Before the synthesis the polymers were dried under vacuum at 40°C. MDI was purified by recrystallization.

Networks were prepared by one-stage process. The initial concentrations of reactive groups in the samples used in this studies vary as

$$[\mathrm{OH}]_{\mathrm{PBD}} : [\mathrm{NCO}]_{\mathrm{MDI}} : [\mathrm{OH}]_{\mathrm{POPT}} = 1 : x : (x-1)$$

where $x = 1.1$–70 (cf. *Table 1*). After 15 min mixing in nitrogen atmosphere at 60°C, 0.001 wt% catalyst (dibutyltin dilaurate) was added and the reaction mixtures were poured into Teflon moulds of rectangular shape. The reaction proceeded at 70°C for 24 h. The prepared samples had a form of films about 1 mm in thickness.

The mass fractions of sol were determined from the mass decrease after a 3-week extraction of the samples in benzene at room temperature. These values are given in *Table 1* together with the composition, optical transparency and density of the samples. The volume fractions of the phases were calculated by assuming no volume change during mixing.

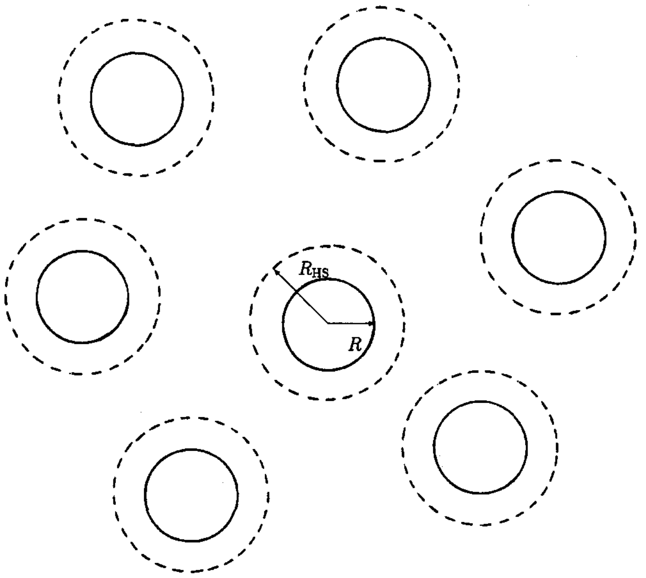

Figure 1 Model of the inhomogeneous structure of polyurethane networks. The model consists of the spherical microdomains of a uniform radius R dispersed in the matrix of major component (POPT/MDI network or PBD) of different electron density. The microdomains interact mutually via hard-sphere interaction characterized by a radius R_{HS}

Table 1 Sample compositions (x is the initial ratio of the isocyanate and PBD hydroxy groups, w_s is the mass fraction of sol, d is the density, and v_1 and v_2 are the volume fractions of PBD and POPT/MDI phases, respectively)

Sample	x	Appearance	w_s	d (g cm)$^{-3}$	v_1	v_2
UR1	1.1	Clear	0.30	0.914	0.96	0.04
UR2	1.5	Clear	0.21	0.923	0.92	0.08
UR3	2	Clear	0.09	0.935	0.87	0.13
UR4	3	Clear	0.03	0.954	0.80	0.20
UR5	5	Opaque	0.04	0.952	0.69	0.31
UR6	9	Opaque	0.03	0.968	0.55	0.45
UR7	30	Clear	<0.01	1.090	0.24	0.76
UR8	70	Clear	<0.01	1.119	0.12	0.88
UR9	–	Clear	<0.01	1.144	0	1

Small-angle X-ray scattering

The synchrotron SAXS experiments were performed with an SAXES optics installed at the BL10C of the Photon Factory, Tsukuba, Japan[12]. Specimens of the thickness of about 1 mm were cut from the films and measured in the temperature-controlled holder. The temperature during the measurement was maintained at 25°C. The scattering intensities were corrected with respect to parasitic scattering and absorption of the samples. Before the calculation of scattering parameters the continuous background intensity I_B (caused by thermal fluctuations in the system) was subtracted from measured intensity using the Vonk empirical formula[13]

$$I_B = A_1 + A_2 q^4 \tag{10}$$

where A_1 and A_2 are constants.

Dynamic mechanical analysis

DMA measurements were carried out using a Rheometrics System 4 instrument. The samples were measured in uniaxial elongation at the frequency 1 Hz while heating with the rate of 1°C min^{-1}.

RESULTS AND DISCUSSION

The samples prepared were opaque or transparent according to the composition (see *Table 1*). The opaqueness was observed for the samples UR5 and UR6, containing 55 and 69 vol% of PBD, respectively, where two phases are thought to be comparable with respect to volumes. The rest of the samples were optically clear. The density of the polymers was found to decrease monotonously with increasing the amount of PBD. The mass fraction of sol is quite high in the samples with a higher amount of PBD, probably due to incomplete reaction. It decreases with decreasing the amount of PBD as the concentration of reactive groups increases.

Figure 2 shows the scattering profiles from the polyurethane networks listed in *Table 1*. A distinct peak was observed at $q = 0.5$–$0.9\,\mathrm{Å}^{-1}$ in each scattering profile except for the reference POPT/MDI network (UR9). The peaks confirm the presence of a two-phase structure in all samples containing PBD. The peaks are the most distinct for the samples UR4 and UR5 containing 69 and 80 vol% of PBD, respectively. The values of the Bragg spacing D were determined from respective peak positions, as summarized in *Table 2*. The Bragg spacing increases from 73 Å to 123 Å with decreasing content of PBD, taking a maximum at 69 vol% of PBD. When the PBD content is decreased further, the Bragg spacing decreases to 107 Å and remains essentially constant in the lower content of PBD. For $q > q_{\max}$ the scattering intensity scales as q^{-n} with n close to 4 (except for the sample with the lowest content of PBD–UR1). This exponent is typical for well separated structure developed in late stages of the phase separation process. In the highest q region the scattering intensities are fitted by the Vonk formula [cf. equation (10)].

All correlation functions for two-phase samples [see equation (3)] have a similar form characterized by damped oscillations but differ in the position of the secondary maxima. As an example, the correlation

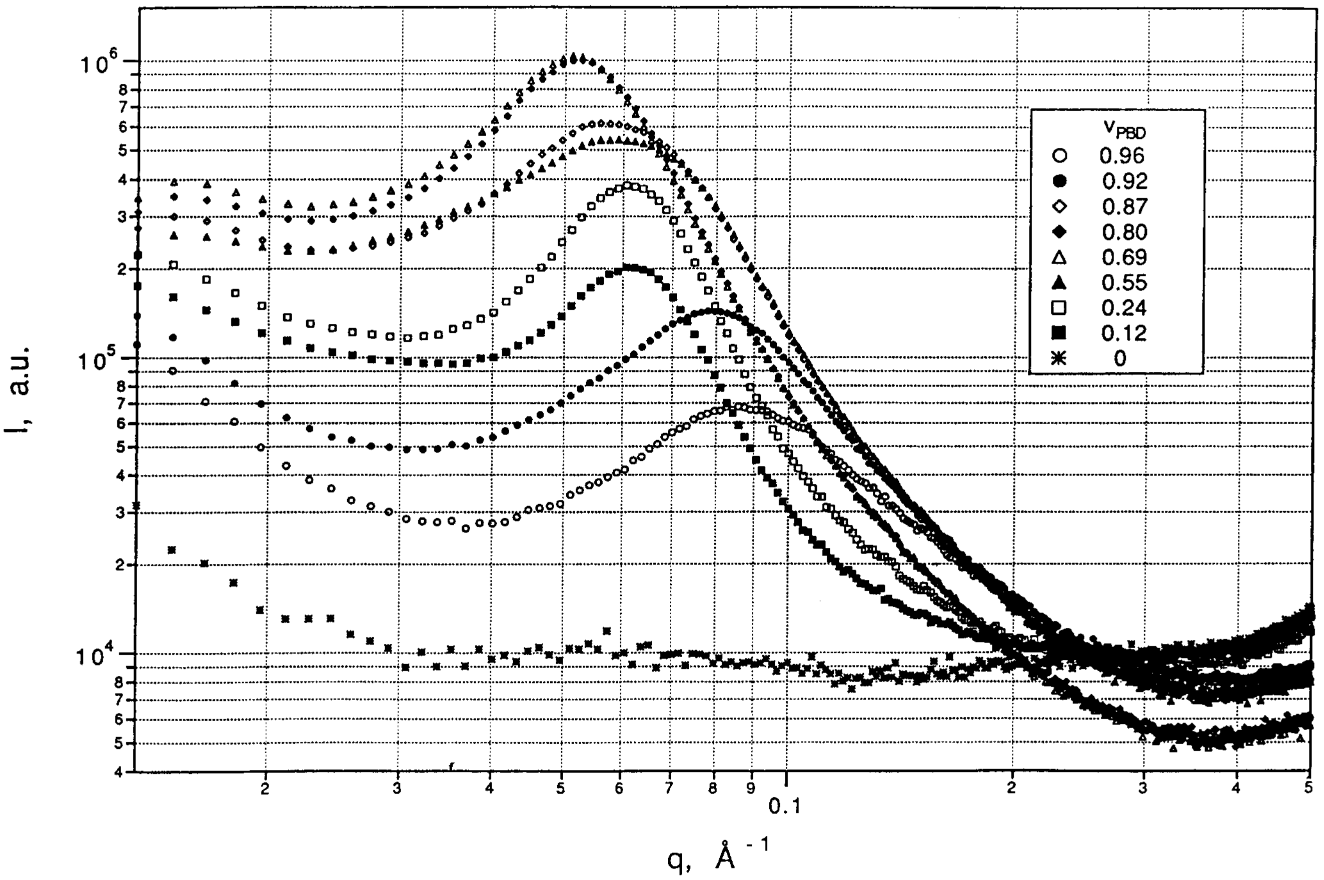

Figure 2 SAXS patterns of the polyurethane polymers (scattering intensity I in arbitrary units vs magnitude of the scattering vector q)

function for the sample UR3 is shown in *Figure 3*. The strong suppression of the oscillations in the correlation function indicates the broad distribution of interdomain spacings.

Figure 4 shows the DMA diagrams, i.e., the temperature dependences of the loss tangent in inhomogeneous polyurethane networks. Two distinct transitions are observed in the diagrams of the opaque samples. Here, the lower temperature transition is attributed to PBD and the higher temperature to the POPT/MDI network. The transparent samples exhibit a single transition corresponding to the dominant phase. This is in accordance with the conjecture that the two-phase structure is observed mechanically or thermodynamically (for example by DMA or d.s.c.[14]) only when the microdomains possess the size in a certain range.

DMA results confirm that one phase in the present systems consists of PBD chains, while the other of densely crosslinked POPT/MDI networks. Except for the samples with the highest content of PBD, the estimated degree of phase separation decreases with decreasing the amount of PBD as can be seen from the values of the ratio $Q/(v_1v_2)$ in *Table 2*. Due to the polarity of terminal PBD hydroxy groups the PBD chain ends are considered to be located mainly on the interphase boundary.

Table 2 Calculated SAXS parameters. $Q/(v_1v_2)$ is the degree of phase separation, D is the Bragg spacing

Sample	$Q/(v_1v_2) \times 10^{-6}$ (a.u. Å^{-3})	D (Å)
UR1	11	73
UR2	9.0	81
UR3	11	112
UR4	6.5	119
UR5	4.8	123
UR6	4.7	107
UR7	3.1	103
UR8	2.7	103

The observed scattering intensities from the transparent samples were fitted using the Percus–Yevick hard-sphere model. To obtain good fits the assumption about the inequality of microdomain and hard-sphere interaction radius was necessary. The comparison of the experimental and calculated SAXS profiles is shown in *Figures 5a–f*.

The fits in the proximity of the scattering peak are satisfactory. However, at higher q values the model gives values exhibiting damped oscillations and lower than those observed experimentally. The oscillations are caused by intradomain scattering due to the spherical shape of microdomains. The calculated values of the fitted parameters are given in the first half of *Table 3*. The microdomain radius R as well as the hard-sphere interaction radius R_{HS} increase with decreasing the content of PBD until the phase inversion takes place. The values of the volume fraction of hard spheres (v) seem also to grow with decreasing the content of PBD. If the Percus–Yevick model coupled with a sphere scattering factor were adequate for the present system, the values of the ratio $(R/R_{HS})^3v$ (given in the fifth column

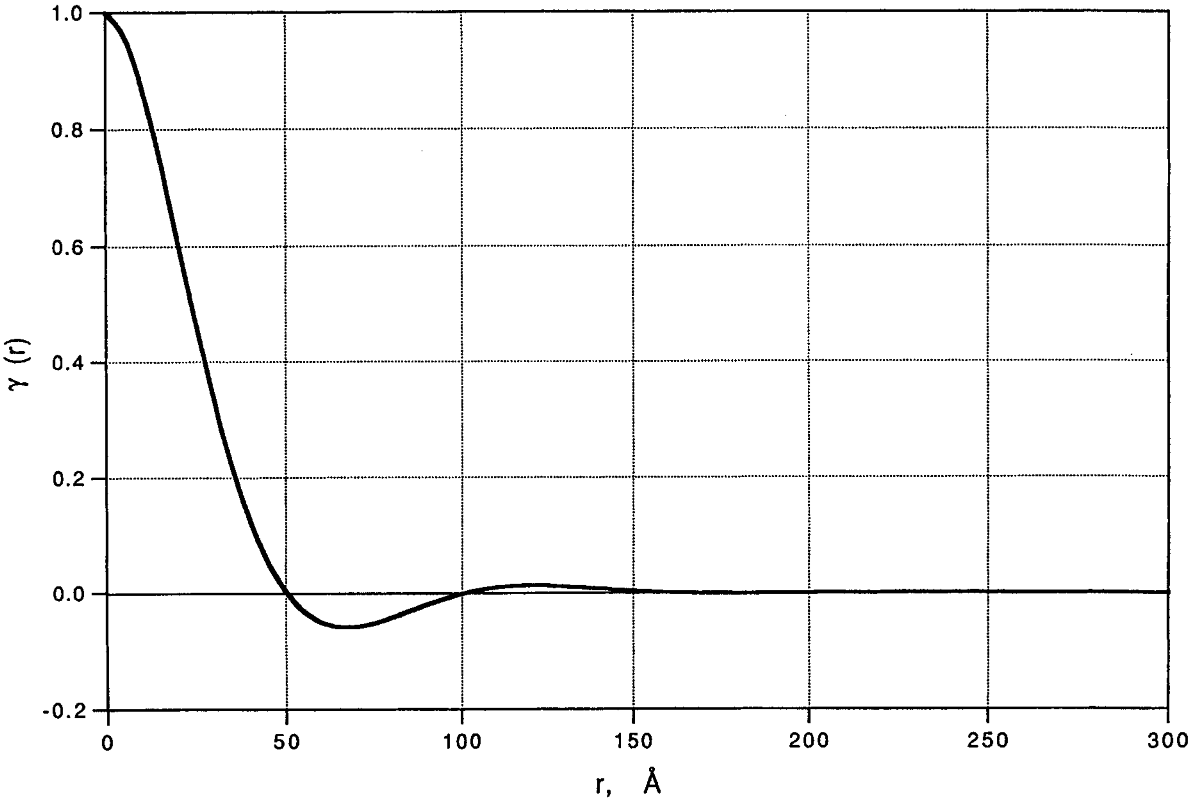

Figure 3 Correlation function of the electron density fluctuations $\gamma(r)$ calculated for the sample UR3 [cf. equation (2)]

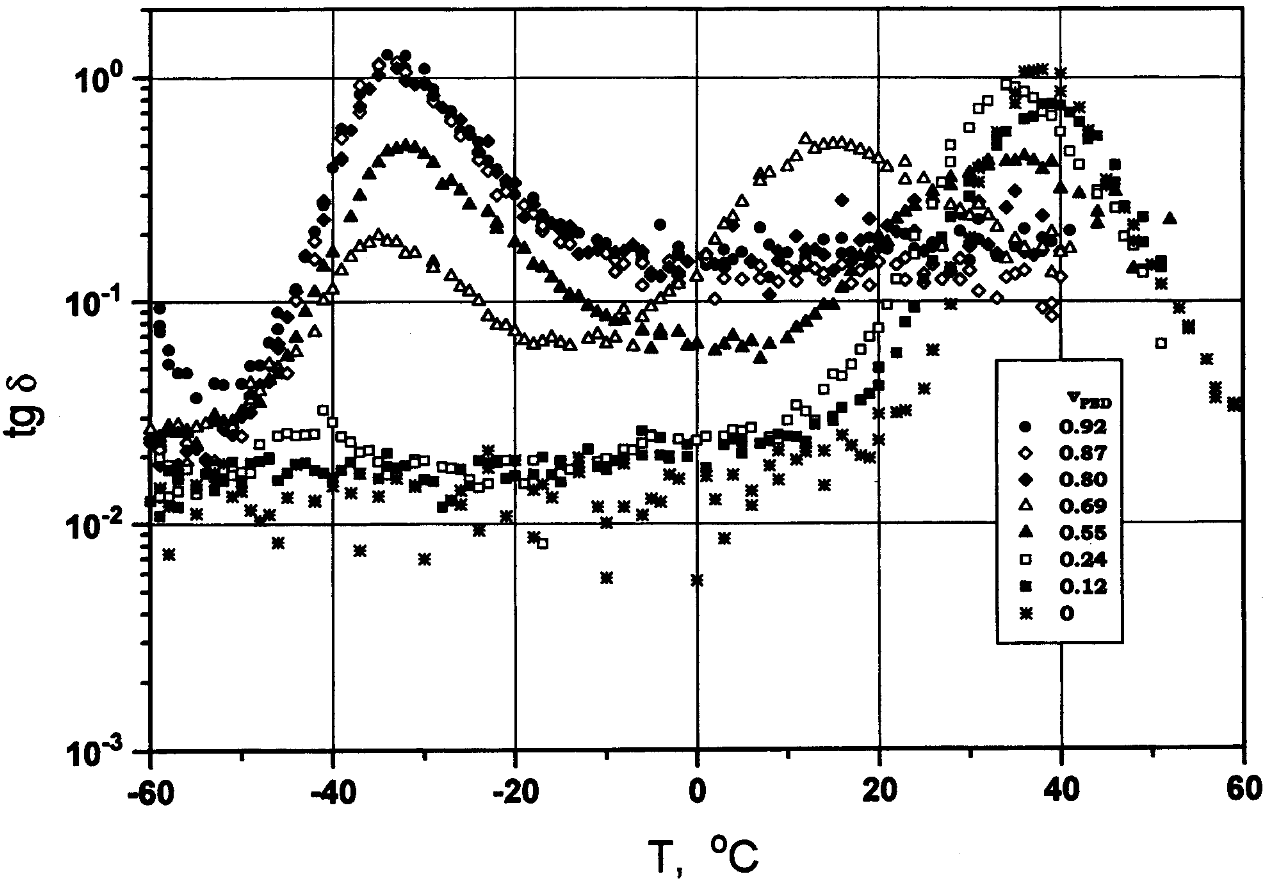

Figure 4 The temperature dependence of the loss tangent

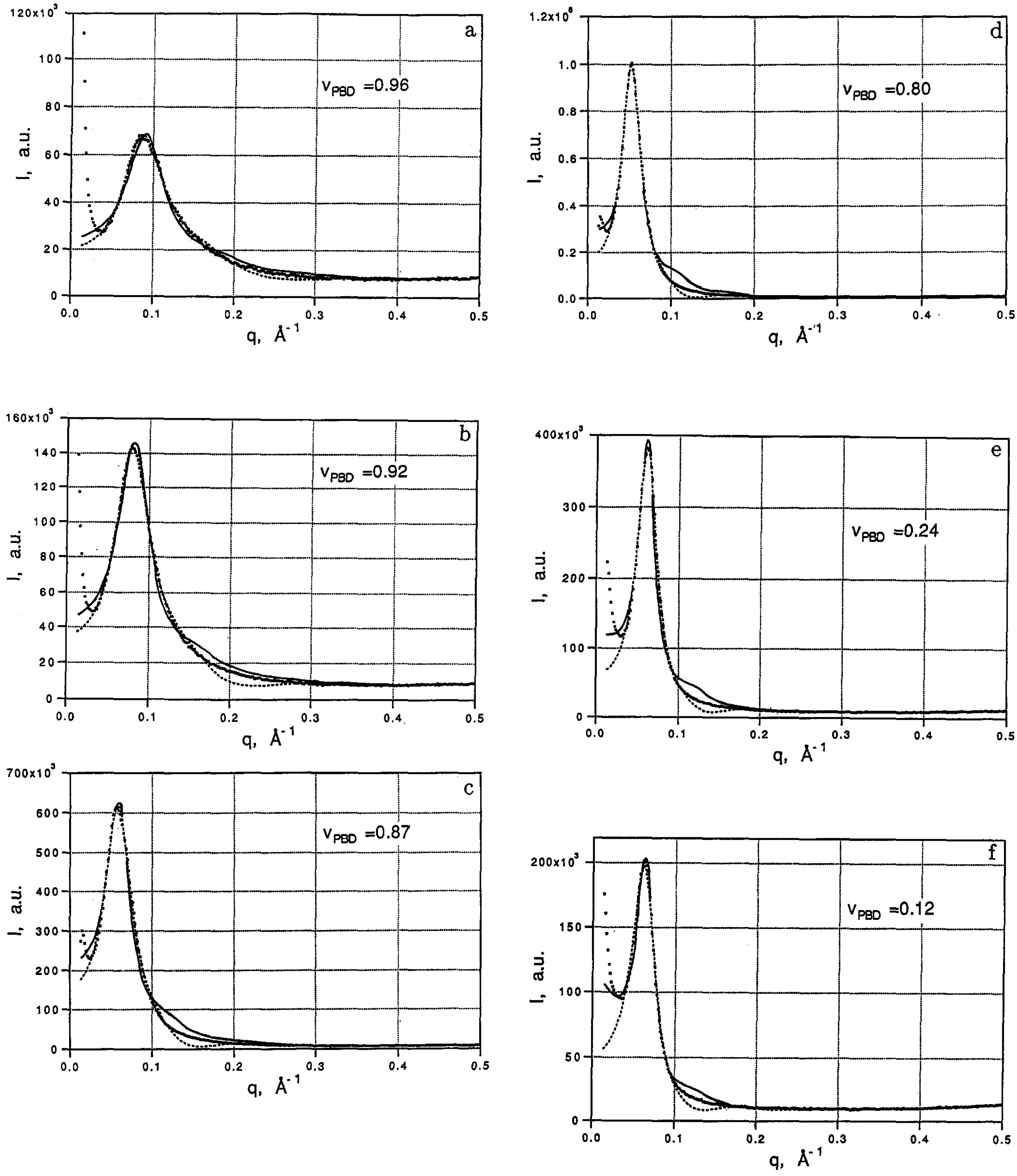

Figure 5 (a–f) Comparison of the experimental (■) and theoretical SAXS patterns calculated by using scattering factor for a sphere (- - -) and scattering factor of Debye–Bueche type (——)

of *Table 3*) should be equal to the values of the volume fraction of minor phase. It can be seen that the former are much lower than the latter.

Therefore, in the second approach we have abandoned the assumption about the sharp surface of microdomains and the scattering factor given by equation (7). We assumed the microdomains without sharp boundary, with more general electron density distribution leading to the scattering factor of the Debye–Bueche type

$$P(q, a_{\text{con}}) = \frac{1}{(1 + a_{\text{cor}}^2 q^2)^2} \tag{11}$$

where a_{cor} is a correlation length specifying the electron density fluctuations in one microdomain.

The interaction between such microdomains was

Table 3 'Best-fits' of SAXS profiles for transparent samples using sphere and Bueche–Debye type scattering factors. (R is the radius of a microdomain assuming spherical shape, a_{cor} is the correlation length, R_{HS} is the hard-sphere interaction radius and v is the volume fraction of hard spheres)

	Sphere type				Debye–Bueche type		
Sample	R, Å	R_{HS}, Å	v	$(R/R_{HS})^3 v$	a_{cor}, Å	R_{HS}, Å	v
UR1	16	33	0.21	0.024	8	32	0.24
UR2	19	37	0.23	0.031	10	36	0.27
UR3	28	48	0.22	0.044	16	48	0.27
UR4	35	56	0.27	0.066	21	56	0.32
UR7	32	49	0.30	0.084	21	49	0.34
UR8	33	47	0.27	0.093	24	48	0.33

assumed to be again of the hard-sphere type. The 'best-fit' results are also shown in *Figures 5a–f* and the calculated parameters are given in the second half of *Table 3*.

Both the correlation length a_{cor} and the hard-sphere radius R_{HS} again increase with decreasing the content of PBD until the phase inversion takes place.

It can be seen that the 'best-fit' values of the hard-sphere interaction radius and volume fraction of hard spheres are close to those calculated assuming the sphere scattering factor. This is reasonable as the maxima in scattering patterns which determine the values of these parameters are relatively sharp.

In the proximity of the scattering peak the fits are also satisfactory. However, at higher q values the model gives values higher than those observed experimentally. In this area the form of the scattering pattern calculated is sensitive to the form of (repulsive) interaction between domains and the hard-sphere interaction seems to be too crude. Nevertheless, we think that the model proposed is able to give at least a qualitative description of the system studied.

CONCLUDING REMARKS

An inhomogeneous two-phase structure of polyurethane networks prepared from PBD, MDI and POPT has been revealed by SAXS. The interdomain distance was estimated as about 70–130 Å from the Bragg spacing, and was found to assume the longest distance at about 70 vol% of PBD in the network. The observed intensities can be fitted well by using a Percus–Yevick hard-sphere model incorporated in the Debye–Bueche particle scattering function. The degree of the phase separation, as estimated from the value of the scattering invariant, decreases with decreasing the amount if PBD. The samples are transparent or opaque depending on the content of PBD. The opaqueness occurs at about 40–75 vol% of PBD. Two transitions corresponding to PBD and POPT/MDI phase were observed by DMA in the opaque samples. The transparent networks consist of the microdomains formed by minor components dispersed in the matrix of major components. The size of the microdomains is too small to be observed by DMA.

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