

## Dynamic mechanical behaviour of random copolymers of a LC-methacrylate and octyl methacrylate

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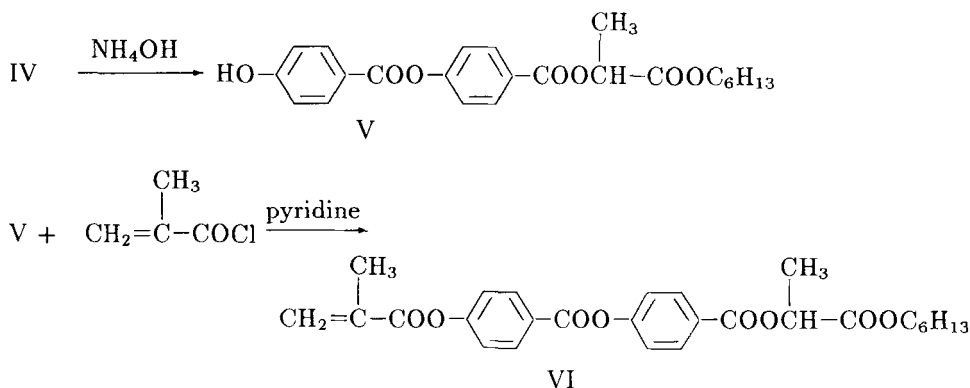
### Summary

The dynamic mechanical behaviour of random copolymers of LC monomer - 1-(hexyloxy-carbonyl)ethyl 4-[4-(methacryloyloxy)benzoyloxy]benzoate (HB) and octyl methacrylate (OMA) was studied in the main transition and flow regions. Even though the aliphatic end groups of the side chain of HB and OMA are roughly the same, the  $T_g$  temperature of poly(HB) is  $\sim 80$  K higher than that of poly(OMA); this fact is due to the presence of the stiff phenyl benzoate mesogenic group in the side chain of HB. With increasing content of OMA in the copolymer the superimposed curves of the storage  $G'_p$  and loss  $G''_p$  moduli at a constant temperature shift towards shorter frequencies. It has been shown that this shift is mainly due to an increase of the free volume in the copolymers with increasing content of OMA. While HB monomer shows liquid crystalline (LC) properties, its polymer (poly(HB)) and random copolymers with OMA show only isotropic thermal behaviour because no flexible spacer is present in the side chain of HB which would decouple the main chain and mesogenic group motions. This means that neither the homopolymer of HB, nor its copolymers with a flexible comonomer retain the LC properties of the starting LC monomer, HB.

### Introduction

Copolymerization of two monomers is one of the effective methods of modification of physical properties of polymers (1–3). It was found that the temperature and frequency (time) dependences of dynamic (static) mechanical functions are sensitive to the homogeneity of the copolymer structure: while a random copolymer shows one main transition, a block copolymer undergoes two. The loss of the block character usually leads to a single, though broad transition; in such a case the behaviour is thermorheologically complex and the time-temperature superposition cannot be performed (4,5). On the other hand, viscoelastic behaviour of random copolymers is rather simple and was investigated for many systems from the point of view of the dependence of glass transition temperature and of the shape and position of mechanical functions of frequency on the composition of the copolymer. It was usually found that in random copolymers free or specific volumes of components are additive and at  $T_g$  the free volume attains a critical value (the free volume theory). The agreement of theory with experimental data has been found for poly(2-hydroxyethyl





Hexyl 2-(4-hydroxybenzoyloxy)propanoate (III) was prepared by the reaction of hexyl L-lactate with the protected 4-hydroxybenzoyl chloride I (12). The product boils at 190–195°C/130 Pa,  $[\alpha]_D = +23.5^\circ$  (20% solution in EtOH).

IV and V were prepared similarly to compounds II and III. V is yellow liquid,  $[\alpha]_D = +14^\circ$  (20% solution in  $\text{CH}_2\text{Cl}_2$ ).

Synthesis of 1-(hexyloxy-carbonyl)ethyl 4-[4-(methacryloyloxy)benzoyloxy]benzoate (VI): To a mixture of V (0.12 mol), pyridine (50 ml) and  $\text{CH}_2\text{Cl}_2$  (250 ml), methacryloyl chloride (15 ml) and 0.5 g hydroquinone were slowly added at 0°C. After 36 h the reaction mixture was washed with a solution of sodium carbonate, water, 5% acetic acid and again twice with water. The organic layer was dried over anhydrous sodium sulfate and the solvent was removed by evaporation under reduced pressure. The yield of VI was 60 g;  $[\alpha]_D = +10.0$  (20% solution in  $\text{CH}_2\text{Cl}_2$ ). Elemental analysis: for  $\text{C}_{27}\text{H}_{30}\text{O}_8$  (482.75), found/calculated 66.45/67.2% C, 6.15/6.30% H.

Octyl methacrylate (Union Carbide) was distilled under vacuum.

#### Sample preparation

Radical solution copolymerization of VI (HB) with octyl methacrylate (OMA) was performed with 2,2'-azobisisobutyronitrile (ABIN) in absolute benzene in nitrogen atmosphere. Reaction conditions:  $[\text{HB}] + [\text{OMA}] = 1 \text{ mol/dm}^3$ ,  $[\text{ABIN}] = 0.01 \text{ mol/dm}^3$ , reaction temperature  $T_r = 60^\circ\text{C}$ . After 48 h, the copolymers were precipitated into an excess of methanol, isolated and dried at room temperature at 20 Pa. The products were reprecipitated from 20% solution in benzene into a fivefold excess of methanol, filtered and dried at room temperature at 20 Pa (Table 1).

Their number ( $M_n$ ) and the weight ( $M_w$ ) averages of molecular weights were determined by the GPC method calibrated to PS standards (solvent THF, Table 1).

#### Dynamic mechanical and DSC measurements

Dynamic mechanical behaviour was measured with a Rheometrics dynamic spectrometer (RDS). Small-strain oscillatory shear measurements were performed with parallel-plate geometry with strains between  $\gamma = 0.2$  and 0.001 (linear viscoelasticity). The angular rate  $\omega$  varied from  $10^{-1}$  to  $10^2 \text{ rad}\cdot\text{s}^{-1}$  and temperature was from  $-50$  to  $150^\circ\text{C}$ . While at the beginning of the main transition the plates 10 mm in diameter were used, in the rubbery-plateau and flow regions 25 mm plates were used. During measurement at constant temperature, strain was decreased with

Table 1: Mechanical characteristics of the copolymers

Code	$x_{\text{OMA}}^a$	$M_n^b \cdot 10^{-5}$	$M_w^b \cdot 10^{-5}$	$\rho$ g·cm <sup>-3</sup>	$T_m$ K	$\log \omega_m$ rad·s <sup>-1</sup>	$T_g$ K	$f_g$	$\alpha_f$ K <sup>-1</sup>	$\log a_0$
S1	0	2.5	9.7	1.094	374	0.91	327	0.0254	3.41	0.0
S2	0.2	1.8	6.2	1.058	354	2.21	310	0.0253	3.03	3.57
S3	0.4	1.5	5.2	1.021	338	3.22	298	0.0287	3.93	5.10
S4	0.6	1.5	4.9	1.008	321	4.07	292	0.0303	3.15	6.49
S5	0.8	1.2	3.7	0.995	303	4.88	277	0.0315	3.52	7.80
S6	1.0	1.0	2.9	0.980	277	6.00	251	0.0304	3.95	9.28

<sup>a</sup> Molar fraction of octyl methacrylate monomer in the copolymer

<sup>b</sup> Determined by GPC in THF (polystyrene standards)

increasing  $\omega$ . The real  $G'$  and imaginary  $G''$  components of the complex shear modulus  $G^*$ , and loss tangent  $\text{tg } \delta$  ( $= G''/G'$ ) were determined.

By applying the frequency-temperature superposition to the data, superimposed curves of  $G_p' = G' \cdot b_T$ ,  $G_p'' = G'' \cdot b_T$  and  $\text{tg } \delta_p = \text{tg } \delta$  versus reduced frequency  $\omega \cdot a_T$  shifted to the temperature  $T_0 = 100^\circ\text{C}$  were obtained for all copolymers. The horizontal shift factor  $a_T$  was obtained mainly from  $\text{tg } \delta$  superposition (for  $\text{tg } \delta$  no vertical shift  $b_T$  is necessary). From the temperature dependence of  $\text{tg } \delta$  measured at  $f = 1$  Hz, the temperature of maximum  $T_m$  was determined for individual samples (Table 1). The frequency of maximum  $\omega_m$  of samples was determined from the dependence of superimposed  $\text{tg } \delta$  curves on the reduced frequency  $\omega \cdot a_T$  (Table 1).

The glass transition temperatures  $T_g$  were measured with a DSC calorimeter Perkin-Elmer DCS-2. Prior to measurement, thermal history of all samples was unified by heating to 425 K and cooling down at a rate 10 K·min<sup>-1</sup>. Specific heat  $c_p$  was measured at the same heating rate;  $T_g$  was determined from the point of intersection of tangent in the inflection point and the extrapolated  $c_p$  dependence in the glassy state (onset of the transition, Table 1). Density  $\rho$  was determined by weighing in water and in air (Table 1).

## Results and discussion

### Temperature dependences

While monomer HB is partially crystalline and exhibits a liquid-glass transition ( $T_g = 207$  K) and LC behaviour with three transitions at 245 K (cr/sm), 260 K (sm/n) and 273 K (n/i, total enthalpy change  $\Delta H = 131$  J·g<sup>-1</sup>), its polymer (poly(HB)) is amorphous and shows only the glass transition ( $T_g = 327$  K, Fig. 1). The polymer behaviour is due to the absence of any flexible spacer in the side chain of monomer HB which would decouple the main chain motion from mesogenic group. Similar thermal behaviour, typical for amorphous structure, was observed for all the copolymers. Thus the introduction of flexible OMA units into the polymer chain does not allow the arrangement of the side-chain phenyl benzoate mesogens to form LC phases in copolymer.

Even though the aliphatic end groups of the side chain of OMA and monomer HB are comparable, the  $T_g$  temperatures of their polymers differ more than 80 K (Table 1). The higher  $T_g$  value of poly(HB) is due to the presence of the stiff phenyl benzoate

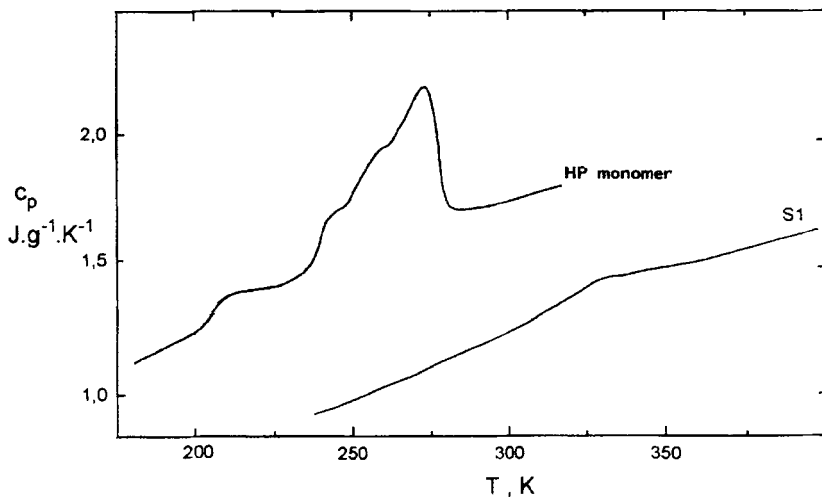


Figure 1: DSC curves of HB monomer and of copolymer S1, heating rate 10 K/min

moiety in the side chain. From Table 1 it follows that  $T_g$  temperatures of copolymers decrease roughly linearly with increasing molar fraction of OMA,  $x_{\text{OMA}}$ . The same linear decrease can be seen in the dependence of  $T_m$  temperatures ( $T_m \sim T_g + 30$  K) on the composition. These linear dependences on composition indicate that the molar volumes in the copolymers are additive.

The temperature dependences of the horizontal shift factors,  $\log a_T$ , of all the copolymers follow the WLF equation in the form (3)

$$\log a_T = -[1/(2.3f_0)](T - T_0)/(f_0/\alpha_f + T - T_0) \quad (1)$$

where temperature  $T_0 = 100^\circ\text{C}$ ,  $f_0$  and  $\alpha_f$  are the fractional free volume at  $T_0$  and the thermal expansion coefficient of the free volume, respectively. It is interesting to mention that the values of  $\alpha_f$  are practically independent of composition of the copolymers ( $\alpha_f \sim 3.5 \times 10^{-4} \text{ K}^{-1}$ , Fig. 2). As expected, the free volume  $f_0$  values increase with increasing  $x_{\text{OMA}}$  due to the increase in the  $T_0 - T_g$  differences. If the  $f_0$  values are shifted to the  $T_g$  temperatures of individual copolymers, then corresponding  $f_g$  values are almost constant ( $f_g \sim 0.028$ , Table 1). These  $f_g$  and  $\alpha_f$  values correlate well with the universal values (3) ( $f_g = 0.025$  and  $\alpha_f = 4.8 \times 10^{-4} \text{ K}^{-1}$ ).

#### Frequency dependences

With increasing content of OMA,  $x_{\text{OMA}}$ , the superimposed curves of both reduced moduli,  $\log G'_p$  and  $\log G''_p$  at  $T_0 = 373$  K, are shifted to higher frequencies  $\omega \cdot a_T$  by about 5 decades, practically without change in their shape (Fig. 3). This means that the values of the monomeric friction coefficient  $\xi_m$  which, in agreement with Rouse's modified theory (3), characterize the position of the moduli on frequency axes, decrease with increasing content of OMA component. Since the dependence of the  $\xi_m$  on temperature, pressure and length of the side chain in a homologous series of poly(alkyl methacrylates) could be expressed quantitatively as a change of the free volume (3), the same concept was used for description of the dependence of  $\xi_m$  on

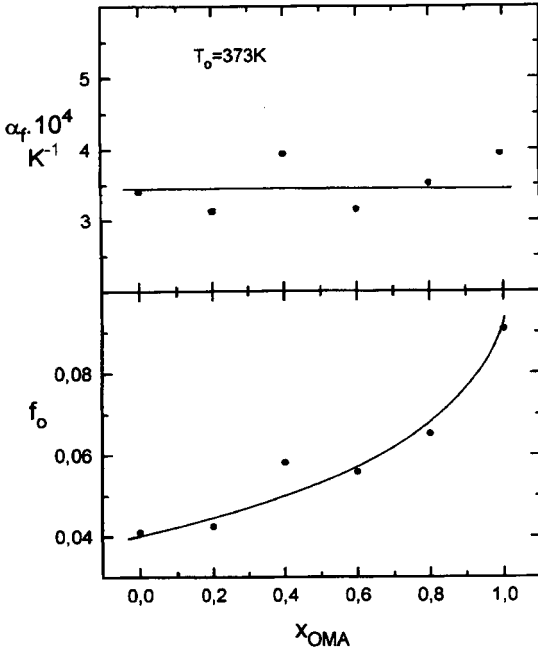


Figure 2: The dependence of the fractional free volume,  $f_0$ , and of the thermal expansion coefficient,  $\alpha_f$ , on the mole fraction of OMA in the copolymer,  $x_{OMA}$

composition of random copolymers (6). To ascribe the shift of mastercurves of moduli to a change in the free volume with the composition of copolymers, it is necessary to

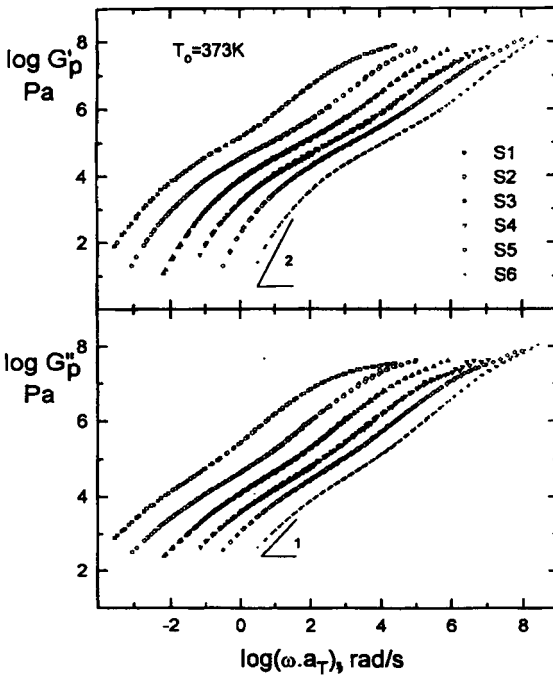


Figure 3: The dependence of superimposed storage,  $G'_p$  (Pa), and of loss,  $G''_p$  (Pa), moduli on reduced frequency  $\omega \cdot a_T$  ( $\text{rad} \cdot \text{s}^{-1}$ )

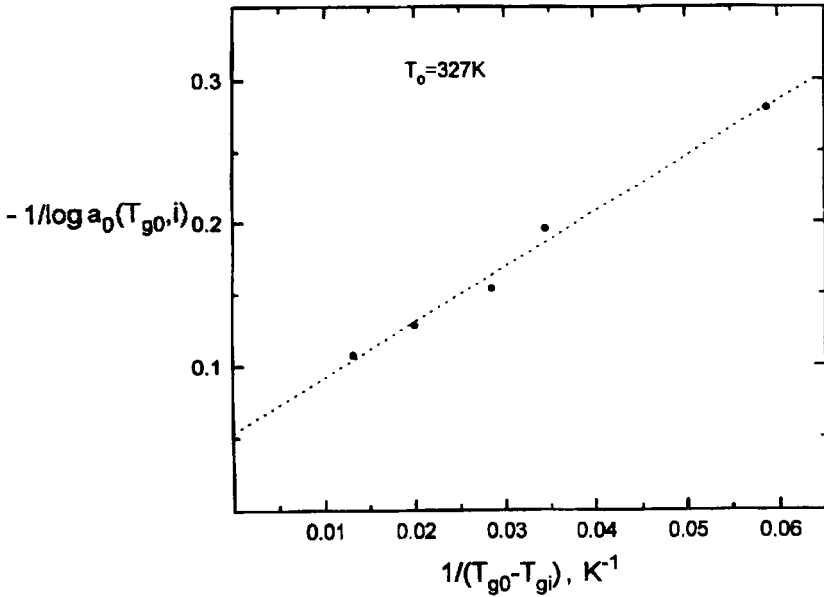


Figure 4: The dependence of  $1/\log a_0(T_{g0}, i)$  from Eq.(2) on  $1/(T_{g0} - T_{gi})$

verify if the relationship

$$-1/\log a_0(T_{g0}, i) = 2.3f_g(T_{g0}) + 2.3[f_g(T_{g0})]^2/[\alpha_{fi}(T_{g0} - T_{gi})] \quad (2)$$

is satisfied (6,8). In this equation,  $f_g(T_{g0})$  is the fractional free volume of polymer poly(HB) at its  $T_{g0}$  temperature ( $f_g(T_{g0}) = f_g = \text{const}$ ),  $\alpha_{fi}$  is the thermal expansion coefficient of the free volume of the  $i$ -th copolymer which has the glass transition temperature  $T_{gi}$  and  $\log a_0(T_{g0}, i)$  (an analogue of the temperature shift factor  $\log a_T$ ) is given by the shift of the  $G'_p$  and  $G''_p$  mastercurves of the  $i$ -th copolymer towards the curves of the poly(HB) polymer (using eq. (1) all mastercurves of moduli were shifted from  $T_0 = 373$  K to  $T_{g0} = 327$  K). Since  $\alpha_{fi}$  values of the copolymers are approximately constant (Table 1), we can plot the values  $-1/\log a_0(T_{g0}, i)$  against  $1/(T_{g0} - T_{gi})$ . As it can be seen from Fig. 4, a linear dependence is obtained and from the  $y$ -intercept and slope the values of  $f_g(T_{g0}) = 0.024$  and  $\alpha_{fi} = 3.2 \times 10^{-4} K^{-1}$  were obtained. Both the constants coincide with the average values which were determined from WLF equation (Table 1). Thus a conclusion can be made that the shift of the viscoelastic curves towards higher frequencies with increasing the OMA content in copolymers is caused by an increase in the free volume. This increase can be, in the first place, ascribed to a higher flexibility of the side chain of OMA monomer. It can be therefore concluded that in various copolymer systems, additivity of the free (or molar) volumes can occur, independently of what the structural causes of the different size of the free volumes of these comonomer units may be.

As can be seen from Figure 3, the increasing content of OMA,  $x_{OMA}$ , shifts the viscoelastic functions to higher frequencies but their shapes remain almost preserved. In the flow region at lowest frequencies, the slopes in these dependences have expected values for Newtonian liquids (3) ( $G'_p \sim (\omega \cdot a_T)^2$  and  $G''_p \sim (\omega \cdot a_T)^1$ ). A detailed

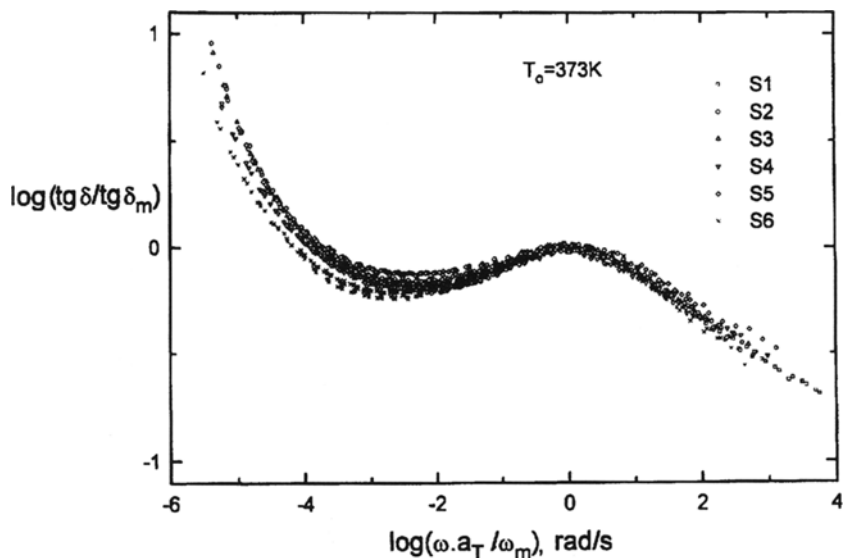


Figure 5: The dependence of the reduced loss tangent,  $\text{tg } \delta / \text{tg } \delta_m$ , on the reduced frequency,  $\omega \cdot a_T / \omega_m$ , for all the copolymers

comparison of the frequency shape for all the copolymers is shown in Figure 5 where the dependences of  $\log(\text{tg } \delta / \text{tg } \delta_m)$  on  $\log(\omega \cdot a_T / \omega_m)$  are plotted ( $\text{tg } \delta_m$  is the maximum value in dependence of  $\text{tg } \delta$  on  $\omega \cdot a_T$ ). Within the experimental scatter, no systematic change in the shape of  $\text{tg } \delta$  curves with composition of the copolymers is seen.

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