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Semifluorinated Methacrylate Random Copolymers: Phase Transitions and Molecular Dynamics

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Random copolymers of methyl methacrylate (MMA) and sermifluorinated methacrylate (sfMA), with constant side chain length ($H_{10}F_{10}$), as comonomers and various sfMA molar contents were studied by Dielectric Relaxation Spectroscopy (DRS) technique with respect to their phase transitions and molecular dynamics. DRS technique was proven a suitable technique for the detection of the phase transitions that take place in the systems under investigation, as it follows from the comparison with Differential Scanning Calorimetry (DSC) technique, which is traditionally used. Regarding molecular mobility, molecular motions of both the main chain and the sf side chains were followed, while different dynamics was recorded depending on the structure of the copolymers.

Keywords Semifluorinated methacrylates; dielectric relaxation spectroscopy; molecular mobility; random copolymers; phase transitions

Introduction

Polymers with semifluorinated (sf) segments have gained much attention over the last 30 years due to their unique properties particularly originating from the tendency of sf segments to self organize into well ordered structures. The simplest example of sf compounds are sf alkanes of the general structure $(CH_2)H_m(CF_2)F_n$. A strong tendency to form a smectic phase has been reported for these systems [1–4]. The tendency of sf segments to get organized in smectic structures have been found to persist when sf chains are attached in polymer backbone as side chains either in form of a sf homopolymer or a sf copolymer [5–11]. The effects of the formation of an ordered structure on the surface of sf polymer thin films on the surface properties such as surface energy and stability have been reported [5–8, 12–14].

In the frame of understanding the structure-property relationships in sf polymers molecular dynamics has been studied by dielectric relaxation spectroscopy technique. Results of molecular dynamics have been reported for sf alkanes [15–16], as well as for various polymers with attached sf chains as side chains either as homopolymers [17–20] or as copolymers [21–23]. The molecular mobility of the chain backbone, as well as that of the sf side chains, ranging from local to segmental motions was followed and related to

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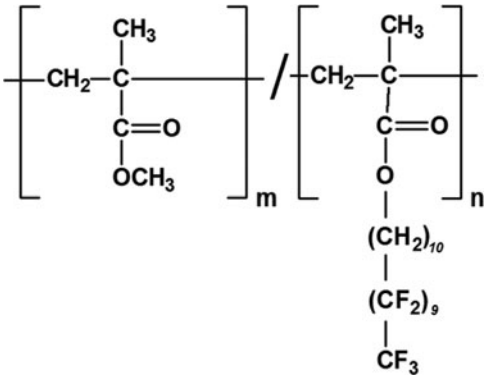

Figure 1. Chemical structure of P(MMA/sfMA) random copolymers

the structure of the systems. For all the systems investigated a common local relaxation of the sf side chain was found, while depending on the system also larger scale motions of the side chains were followed. Additionally, dielectric relaxation spectroscopy technique has been used for the detection of phase transitions in systems that have liquid crystalline behaviour [16, 24].

In the present work phase transitions and molecular dynamics in random copolymers of methyl methacrylates (MMA) and semifluorinated methacrylates (sfMA), with constant side chain length ($H_{10}F_{10}$), as comonomers and various sfMA molar contents are studied by dielectric relaxation spectroscopy technique. It has been found in previous work that for $H_{10}F_{10}$ methacrylate copolymers with sfMA contents higher than 25mol% the side chains are organized in well ordered layered structures where chain backbone and side chains alternate [25, 26]. Copolymers with sfMA molar contents below 25mol% show only a glass transition, T_g, while for higher contents additionally to the glass transition transitions from isotropic to liquid crystalline, T_i, and from liquid crystalline to crystalline phase, T_m, were found. The structure of the samples was studied by temperature dependent X-ray techniques and published in [26]. A typical smectic structure is formed at $T_m<T<T_i$ and negative coefficient of the linear expansion of the layer distance (4,7 to 4,2 nm) was found. At $T>T_i$ the layer structure is lost. The fluorinated parts of sf side chains was found to be comparable to hexagonally packed Poly(tetrafluoroethylene) chains in helix conformation at $T<T_m$. In the present work both systems with sfMA content lower and higher than 25 mol% are studied in order to relate molecular mobility to the structure, which is a key issue for controlling the properties of these systems. Different molecular mobility was recorded depending on the structure of the systems, while valuable information was extracted regarding molecular dynamics of PMMA, which still attracts scientific interest [27].

Materials

Random copolymers of methyl methacrylate (MMA) and sf side chain methacrylate (sfMA), P(MMA/sfMA), were synthesized by radical copolymerization in Azobisisobutyronitrile (AIBN). The chemical structure is shown in Fig. 1. Samples with different molar contents of sfMA from 11 mol% to 68 mol% were prepared. Pure PMMA was prepared for comparison. Throughout the paper copolymers are characterized by their sfMA content. In order to

prepare films the samples were pressed between polyimide foils in a hot press under 3000Kg for 20s at 150°C for 31, 40, 49 and 68 mol% and at 185°C for PMMA and 11 mol%.

Experimental Techniques

Dielectric Relaxation Spectroscopy (DRS) and Differential Scanning Calorimetry (DSC) techniques were applied for the study of phase transitions in the copolymers with sfMA contents 40 and 49 mol%. For DRS measurements the samples were placed between two brass electrodes, maintaining the distance between them constant at 50 μm with silica fibers, in order to form a capacitor. The capacitor was heated up to 110°C and then cooled down to −150°C with a rate of 2.5°C/min and subsequently heated up to 110°C while the dielectric response was recorded continuously at 100, 10 and 1kHz. For DSC measurements an amount of approximately 5mg of the sample was placed in an aluminum pan heated up to 150°C with a rate of 10°C/min and then cooled down to -50°C with a rate of 3°C/min and subsequently heated up to 150°C with a rate of 10°C/min. DSC measurements were performed under N_2.

DRS technique was used also for the study of molecular dynamics in pure PMMA and random copolymers with 11mol%, 31 mol% and 68 mol%. The capacitors filled with the samples were prepared as described above. The capacitors were heated up to 110°C, cooled down to −150°C with a rate of 2.5°C/min and subsequently the dielectric response was recorded isothermally in a broad frequency range (10^{-1}-10^{6}Hz) at several temperatures between -150° to a maximum temperature of 130°C, depending on the sample.

For DRS measurements the Alpha analyzer in combination with Quatro cryosystem for the temperature control supplied by Novocontrol were used. For DSC measurements Pyris 6 heat flux calorimeter supplied by Perkin Elmer was used.

Dielectric measurements were analyzed using Havriliak-Negami (HN) function

$$\varepsilon^*(f) = Im\left[\frac{\Delta\varepsilon}{\left[1+(if/f_{HN})^a\right]^b}\right]$$

for each relaxation process, where f_{HN} is a characteristic frequency related to the frequency of maxim loss of the relaxation (f_{max}), $\Delta\varepsilon$ is the relaxation strength and a and b are shape parameters. For b = 1 equation describes a symmetrical relaxation (HN function coincides with the Cole-Cole function).

Because of the use of silica spacer to maintain the thickness of the capacitor, there is an uncertainty in capacitor dimensions which affect the absolute values of dielectric quantities; so all the data are normalized to ε'_{inf} (the real part of dielectric function, ε', at −150°C at 1MHz where no relaxation contributes to the dielectric response) [28].

Results and Discussion

Phase Transitions

Phase transitions from isotropic to liquid crystalline (I→LC) and from liquid crystalline to crystalline (LC→Cr) phase during cooling and from crystalline to liquid crystalline

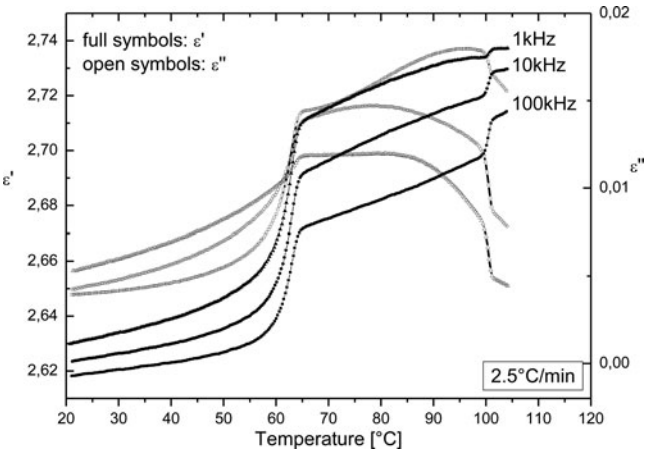

Figure 2. The real and the imaginary part of permittivity, ε' and ε'' on the left and the right axis, respectively, as a function of temperature at three different frequencies noted on the plot during continuous heating of the copolymer with sfMA molar content 40 mol% with a rate of 2.5°C/min.

(Cr→LC) and from liquid crystalline to isotropic (LC→I) phase during heating were followed by DRS and by DSC techniques for the random copolymers with sfMA molar contents 40 mol% and 49 mol%. In Fig. 2 the real part ε' (full symbols) and the imaginary part ε'' (open symbols) of dielectric function are presented as a function of temperature at 100, 10 and 1kHz for the copolymer 40 mol% during heating at a constant rate of 2.5°C/min. The phase transitions Cr→LC and LC→I in order of increasing temperature are followed as frequency independent upward steps in ε' and as sharp changes in ε''. Data of ε'' are included in the plot in order to follow also the molecular mobility present in the temperature range of the experiment. As can be seen there are contributions from dielectric relaxations

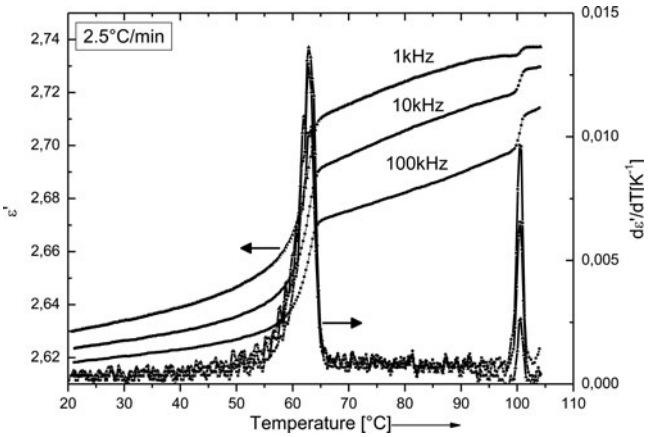

Figure 3. The real part of permittivity, ε' (left axis) and temperature derivative of ε', $d\varepsilon'/dT$ (right axis) as a function of temperature at three different frequencies noted on the plot during continuous heating of the copolymer with sfMA molar content 40 mol% with a rate of 2.5°C/min.

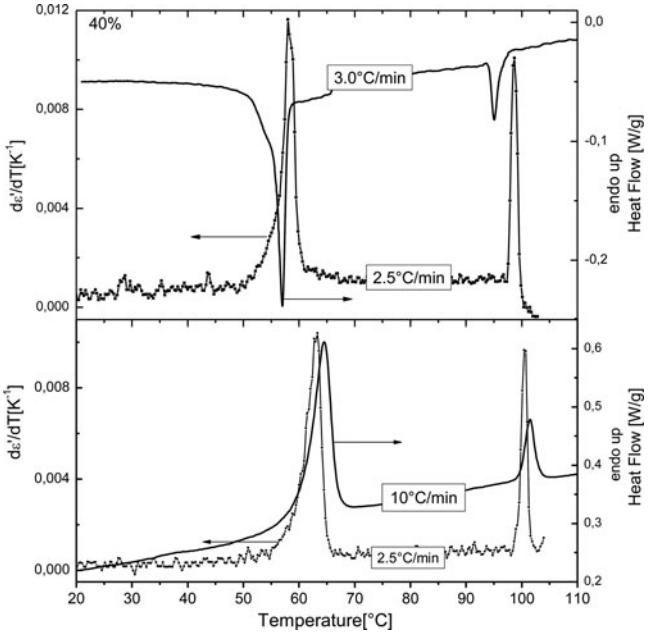

Figure 4. Temperature dependence of the first derivative of ε' from DRS (dε'/dT, left axis) and of heat flow (right axis) for the copolymer 40 mol%. The upper graph is during cooling and the lower during heating with the rates indicated on the plots.

which are frequency dependent and are superimposed on the changes due to the transitions. This is the reason why the shape and the height of the steps in ε' change with frequency. The ε' is a measure of the polarization in the sample. The transitions from an ordered state in three dimensions (Cr) to one of two dimensions (LC) and to a disordered state (I) results in a change in polarization due to the change in molecular mobility and this is reflected in ε'. Due to the contribution from specific molecular motions in the temperature range of the experiment, which will be discussed in detail later, we cannot extract information from the step height.

However, an estimation of the transition temperatures can be done by using the first temperature derivative of ε', dε'/dT. ε' as well as dε'/dT are presented as a function of temperature in Figure 3 for the copolymer with sfMA molar content 40 mol%. In dε'/dT representation the transitions are seen as frequency independent peaks and one can easily estimate in this representation the transition temperatures from peak temperatures.

A comparison between DRS and DSC results regarding phase transitions is done in Figure 4 where the first derivative of ε' from DRS technique (dε'/dT, left axis) and heat flow from DSC technique are presented for the copolymer with sfMA molar content 40 mol% during cooling (upper graph), as well as during heating (lower graph). The results by the two techniques are in very good agreement for both cooling and heating indicating that DRS technique can be used to record the phase transitions in such systems. This is of particular importance in cases where phase transitions are characterized by small enthalpy changes. Similar results were recorded also for copolymer with sfMA molar content 49 mol% measured but not presented here.

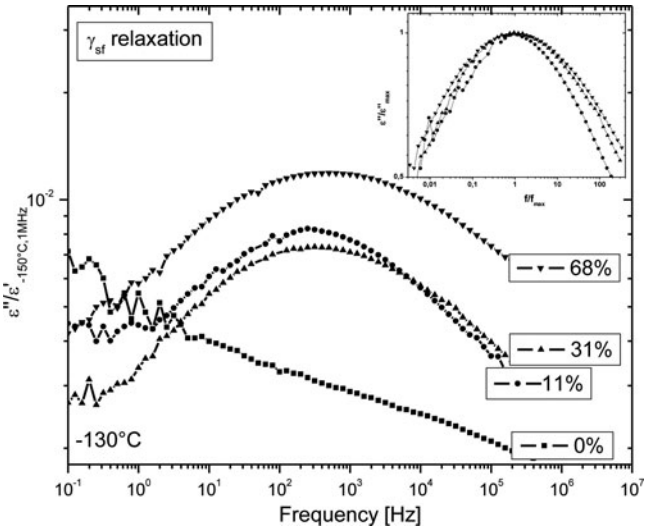

Figure 5. Normalized data of ε'' (see experimental section) as a function of frequency for the samples indicated on the plot at -130°C where the γ_{sf} relaxation can be seen. The inset shows the scaled curves (both in x and y-axes).

Molecular Dynamics

Molecular dynamics was followed for pure PMMA and the random copolymers with molar contents of sfMA 11 mol%, 31 mol% and 68 mol% by DRS technique. Different dynamics was found in copolymers compared to pure PMMA and between the copolymers depending on the structure formed. Each dielectric relaxation which refers to a molecular motion will be presented and discussed regarding its characteristics separately, while their relaxation rates (time scale) will be discussed together for all the relaxations.

γ_{sf} relaxation

For all the random copolymers under investigation a broad relaxation is observed at low temperatures called γ_{sf} relaxation. Figure 5 shows for all the samples the imaginary part of dielectric permittivity,ε'', normalized as described in the experimental section, at -130°C. For pure PMMA no peak is recorded in the temperature region of the relaxation and so the relaxation is attributed to motion in sf side chains. For the samples where side chains are organized (31 mol%, 68 mol%) relaxation has comparable shape but is broader compared to the one in the sample where no ordering is observed (11 mol%), as can be seen in the inset of Figure 5, as well as from the shape parameters extracted from the fitting procedure (not shown here). Measurements at several temperatures show that the relaxation becomes narrower with increasing temperature, which is confirmed and quantified by the shape parameters extracted from the fitting procedure (not shown here). Dielectric relaxation strength increases with increasing the molar content of sfMA, indicating the connection of the relaxation to the sf side chains. Comparable values were found for the copolymers with 11 and 31 mol% of sfMA, while for the sample with 68 mol% the relaxation becomes double. The copolymers where the side chains are organized follow the additive rule, however the values in these samples are lower than those expected taking into account the value observed for the 11 mol%, indicating that the ordering results in a reduction

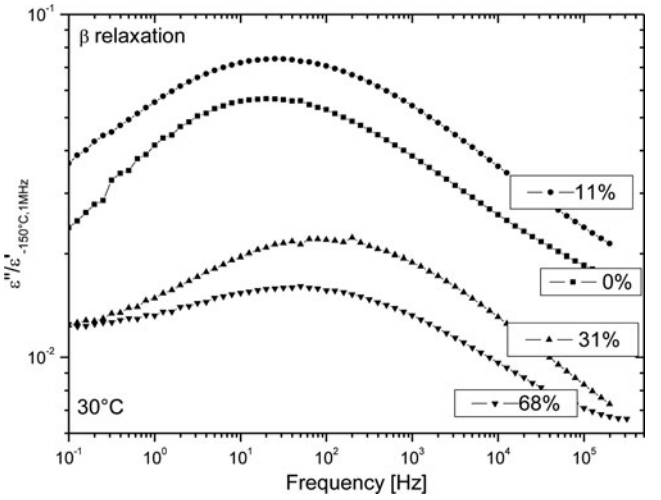

Figure 6. Normalized data of ε'' (see experimental section) as a function of frequency for the samples indicated on the plot at 30°C where the β relaxation of PMMA can be seen.

of dielectric strength due to cancellation of dipole moments. A relaxation with similar characteristics has already been observed in systems having fluoroalkanes as side chains and has been ascribed to motions of CF_3-groups [19, 20, 22, 29].

β and α relaxations

In all the samples including PMMA a broad asymmetric relaxation from sub-T_g far above-T_g temperatures is observed. In Figure 6 the normalized ε'' (see experimental section) as a function of frequency at 30°C for pure PMMA as well as for the copolymers under investigation is shown. In PMMA the relaxation has the same characteristics with the β relaxation of PMMA reported in literature [30]. NMR experiments in PMMA show that β relaxation is related to 180° flips of the pendant carboxyl group around the C—C bond connecting the main chain and the side group, coupled to restricted rocking motion of the chain backbone in order to avoid steric interference from other segments [31]. Relaxation in copolymer with sfMA content 11 mol% resembles that of PMMA, except that it becomes faster in the copolymer. In copolymers with sfMA contents 31 mol% and 68 mol%, where sf chains are organized, the relaxation has different characteristics compared to PMMA. More specifically, in these systems, according to the results of the analysis, the relaxation is slightly narrower, less intense and faster compared to pure PMMA. No significant difference in shape was found for the relaxation between the copolymers with sfMA content 31 and 68 mol%. The dielectric relaxation strength decreases with increasing sfMA molar content for the samples 31 and 68 mol% and is lower than that predicted by the additive rule assuming that only the carboxyl groups connected to MMA contribute to the relaxation. On the contrary, in the copolymer 11mol% relaxation has higher strength than that predicted by the additive rule. In the copolymer 31 mol% the relaxation strength increases steeply when the side chains become isotropic. The molecular environment of the side group is complicated in copolymers compared to pure PMMA and depends on the organization of the sf side chains. In 11 mol% carboxyl pendant groups relax in a similar environment as in PMMA, however the chain packing is looser due to the introduction of the sf side chains

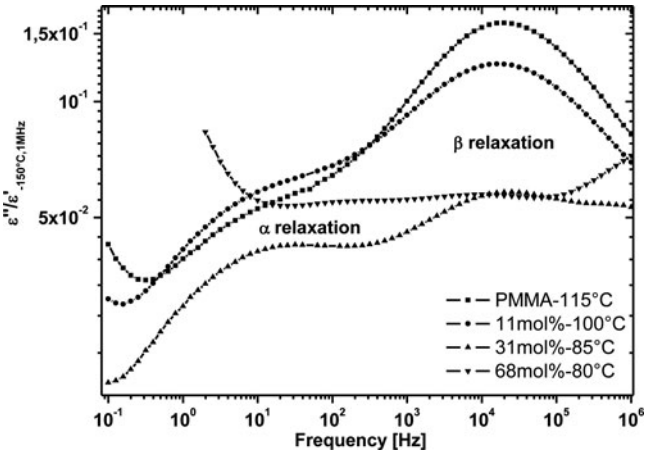

Figure 7. Normalized data of ε'' (see experimental section) as a function of frequency for the samples indicated on the plot. For each sample different temperature is plotted, in order all the samples have comparable relaxation rate of the α relaxation.

and more groups can relax with a higher probability. Faster dynamics for β relaxation of PMMA has been reported in copolymers of PMMA as well as in solutions with toluene [32–34].

At temperatures higher than the glass transition temperature the α relaxation was followed for pure PMMA and copolymers with sfMA molar content 11 mol% and 31 mol%. In Fig. 7 the normalized ε'' as a function of frequency for all the samples under investigation, at different temperature for each one, at which the α relaxation has comparable rate for all the samples, is shown. For the copolymer with sfMA molar content 68 mol% the α relaxation is seen as a peak only at 80°C (Fig. 7), a few degrees higher than the melting temperature. For higher temperatures the α and β relaxations are overlapped and the deconvolution of the peaks is not straightforward. Segmental mobility of the main-chain is possible only above melting temperature for this sample. The α relaxation becomes faster (shifts to higher frequencies/lower temperatures) with increasing sfMA molar content in accordance with the shift of the glass transition to lower temperatures with increasing sfMA molar content found by DSC technique [25]. The relaxation has comparable strength in pure PMMA and copolymer with sfMA molar content 11mol%, while for the copolymer 31 mol% lower values were found. The relative decrease in strength observed for the copolymer 31 mol% is less than that found for the β relaxation.

β_{sf} relaxation

For the copolymers 31 mol% and 68 mol%, in which the sf side chains are organized in layers, an additional relaxation was followed. The evolution of the relaxation with temperature can be followed in Fig. 8 for the copolymer 31 mol%. The fact that the relaxation is observed only when the side chains are oriented suggests that the relaxation is due to the motion of the sf side groups in the phase of the formed layer. The relaxation is observed in crystalline as well as in liquid crystalline phase for the copolymer 31 mol%, while for the copolymer 68 mol% the relaxation can be resolved only in the crystalline phase.

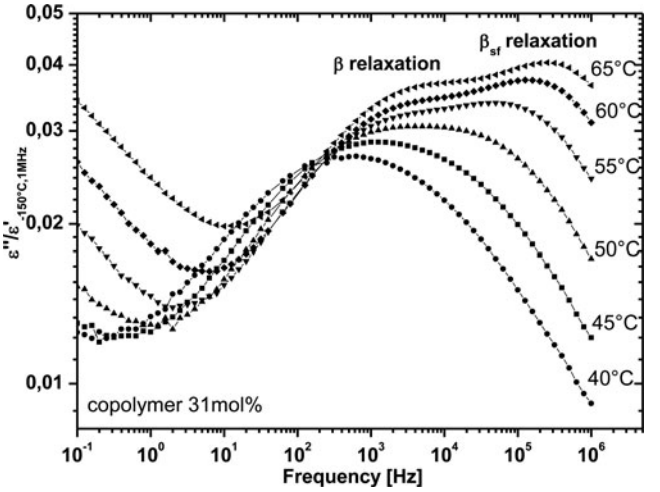

Figure 8. Normalized data of ε'' (see experimental section) as a function of frequency for the copolymer with sfMA content 31 mol% at different temperatures indicated on the plot where the evolution of β and β_{sf} relaxations can be followed.

A relaxation in the same frequency/temperature range has been observed by dielectric spectroscopy in systems with a main-chain of polysulfones and sf side chains identical with those of the present work [20]. The relaxation was assigned there to a glass transition of the domains formed by sf side chains. A similar relaxation was also found by dielectric spectroscopy in the liquid crystalline phase of sf alkane identical to the one used in the present work as side chains and was associated with the rotation of the (CF_2) groups [15].

Temperature Dependence of Dielectric Relaxations

Temperature dependence of the relaxation rates of all the relaxations followed in the samples under investigation is presented in the Arrhenius plot shown in Fig. 9. In the order of increasing temperature/decreasing frequency the traces of the γ_{sf}, β_{sf}, β and α relaxations can be followed. The lines on the plot correspond to the fitting curves with the Vogel-Tammann-Fulcher (VTF) and Arrhenius equations [35]. The behaviour of each relaxation will be discussed separately.

Temperature dependence of γ_{sf} relaxation rate is described by the Arrhenius equation indicating a thermally activated process [35]. Arrhenius equation has been fitted to the data and the resulting lines are shown in Fig. 9. Activation energy is higher for the copolymers where the side chains are organized (31and 68 mol%) equal to 42.9 kJ/mol (0.44eV), compared to 35.6kJ/mol (0.37eV) found for the copolymer with sfMA molar content 11 mol%, where no ordering was detected. Worth mentioning is also that the values for the pre-exponential factor are for all the samples, especially for the copolymers where the side chains are organized, rather high (10^{15}Hz for 11 mol% and 10^{18}Hz for 31 mol% and 68 mol%), not typical for local motions involving exclusively simple energy barriers (e.g. bond rotational potentials, $\sim 10^{12}$ Hz) [35, 36]. Using the Starkweather approach [37] a zero entropy activation energy of approximately 28 kJ/mol was found for all the samples. According to the Starkweather approach the difference between the activation energy calculated from Arrhenius equation and the zero entropy activation energy is equal to the

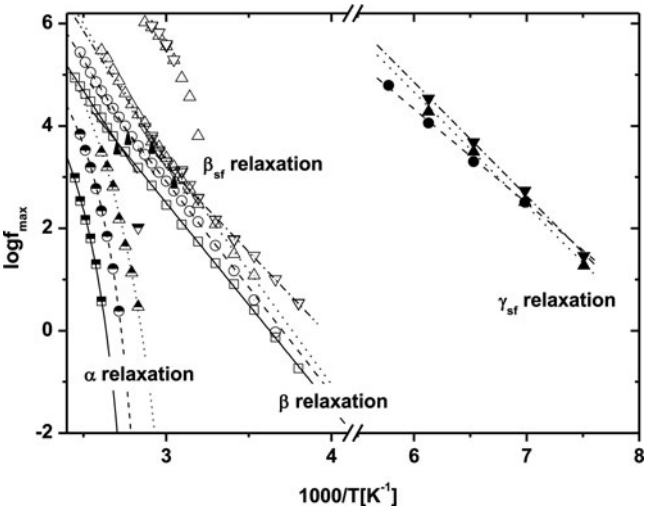

Figure 9. The Arrhenius plot (logarithm of frequency maximum as a function of inverse temperature multiplied by 1000) for all the samples and for all the relaxations observed. The lines are the curves obtained by fitting either with the Arrhenius or with VTF equations. PMMA (squares), copolymer 11 mol% (circles), 31 mol% (up triangles) and 68 mol% (down triangles). Arrows mark the temperatures of change in slope of the trace of the β relaxation.

product $T' \cdot \Delta S$ where T' the temperature at which the maximum of the relaxation is equal to 1Hz and ΔS the activation entropy. A non zero activation entropy was found for all the samples, equal to 0.07 for the copolymer 11 mol% and to 0.12 kJ/mol for the copolymers 31 and 68 mol%. A non-zero value of activation entropy indicates a cooperative character of molecular motion. For many relaxations involving small, sub-molecular fragments moving independently of one another activation entropy is close to zero [37]. Interestingly, for the relaxation in similar copolymers having H_2F_8 as side chains (results not shown here) activation energy of 27 kJ/mol and zero activation entropy were found. According to the study of the structure in copolymers having both $H_{10}F_{10}$ and H_2F_8 as side chains, in the former case the side chains are interdigitized to form the layer, while in the latter are ordered head to head [25, 26]. So, in copolymers with H_2F_8 as side chains the unit can relax independently from the others, while in the copolymers with $H_{10}F_{10}$ as side chains there is a sterical hindrance and in order the unit to relax cooperative motions are needed.

The data for the β relaxation rate can be described by two Arrhenius equations (Fig. 9). The activation energy of the relaxation changes to higher values at high temperatures. The temperatures at which the change occurs (temperature at which the lines are intersected, indicated on the plot by arrows) are close to the glass transition temperatures calculated from the extrapolation of the α relaxation to 1.6 mHz ($\tau = 100$s) [31]. The change in the activation energy of the β relaxation in PMMA at the glass transition temperature is reported in the literature [27, 30] and reflects the coupling of the pendant group to the backbone motion [31]. Interestingly, this behaviour is observed also for the copolymers. The activation energy of the relaxation both below and above the glass transition temperature slightly increases with increasing sfMA molar content. At temperatures below T_g the activation energy increases from 0.79eV for the PMMA to 0.82eV and 0.88eV

for the copolymers 11 mol% and 31 mol%, respectively. At temperatures above T_g the activation energy increases from 0.98 for PMMA to 1.04eV and 1.06eV for the copolymers 11 mol% and 31 mol%, respectively. In the copolymer with sfMA molar content 31 mol% the relaxation remained unaffected by the melting of the side chains, while a small shift of the relaxation to higher frequencies above the isotropization temperature was found. For copolymer with sfMA molar content 68 mol% a change in the activation energy was found at 54°C although the α relaxation was observed only at temperatures higher than the melting temperature of the side chains. For this copolymer the activation energy at temperatures lower than 54°C was calculated equal to 0.67eV, much lower than that in the other systems, while at temperatures above 54°C the activation energy is 1eV close to that observed for the other systems.

The trace of the α relaxation can be followed in Figure 9 for PMMA and the copolymers 11 mol% and 31 mol%. For the copolymer with sfMA molar content 68 mol% only one point is included. The data for the α relaxation are described by the VTF equation with similar parameters for all the samples. For the copolymer with sfMA molar content 31 mol% an insignificant discontinuity of the data is observed at the isotropization temperature, however the same VTF equation describes all the data. The α relaxation shifts to lower temperatures/higher frequencies with increasing sfMA molar content, in accordance with the lower values obtained by DSC for the glass transition temperature. The values found for the dielectric glass transition calculated from the extrapolation of the α relaxation to 1.6mHz ($\tau = 100$s), T_{gdiel}, are in very good agreement with the values obtained by DSC [25]. The shift of the α relaxation to lower temperatures/higher frequencies can be understood in terms of internal plastistization due to the incorporation of the sf side chains.

A shift of the β relaxation of PMMA to lower temperatures/higher frequencies as well as a decrease in its activation energy have been reported for alternated and random copolymers of PMMA with Poly(styrene), PS [34]. In the case of the random copolymers the shift of the relaxation to lower temperatures/higher frequencies is more pronounced as the content of PS increases, while a decrease in activation energy is observed for alternated copolymers and random copolymers with high content of PS. In the same reference no change was found in the corresponding diblock copolymers. Unaffected dynamics of the β relaxation of PMMA have been reported in blends and diblock copolymers of PMMA with PS [38], while, Koizumi et al. [17] reported on the plasticization effect of side chains on the segmental motion of poly(fluoroalkyl methacrylates) and the antiplasticization effect on the side chain motions with increasing side chain length.

Finally, for the copolymers with sfMA molar contents 31 and 68 mol%, where the side chains are organized in layers, the trace of the β_{sf} relaxation can be followed in Figure 9. For the copolymer with sfMA molar content 31 mol%, for which the relaxation can be followed for sufficient number of temperatures, relaxation rate can be described either by the VTF equation or by two Arrhenius equations. However, first derivative of the data (not shown here) suggests a change of the behaviour at 50°C, which is close to the melting temperature of the side chains and where the lateral arrangement observed by WAXS technique disappears. For the copolymer 68 mol% the β_{sf} relaxation can be followed only for few temperatures. The relaxation contributes to dielectric response also at lower temperatures, but it is not easy to extract data by fitting. The existence of the relaxation at lower temperatures emerges as scattering in the data of the β relaxation in this region. The time scale of the relaxation is the same for both systems. However, the relaxation has the same rate, although the side chains are in different states, liquid crystalline in copolymer with sfMA molar content 31 mol% and crystalline in copolymer with sfMA content 68

mol%, which suggests that the relaxation is not affected by the organization of the side chains.

Conclusions

In the present work random copolymers of methyl methacrylate (MMA) and sermifluorinated methacrylate (sfMA), with constant side chain length ($H_{10}F_{10}$), as comonomers and various sfMA molar contents were studied by Dielectric Relaxation Spectroscopy (DRS) technique with respect to their phase transitions and molecular dynamics.

DRS technique was proven a suitable technique for the detection of the phase transitions, that take place in the systems under investigation, as it follows from the comparison with Differential Scanning Calorimetry (DSC) technique, which is traditionally used for the detection of phase transitions.

Molecular motions of both the main chain and the sf side chains were followed in the copolymers, while different dynamics was recorded depending on the structure of the copolymers. The main α relaxation related to the glass transition of the system was found to shift to lower temperatures/higher frequencies with increasing sfMA content, in accordance with the decrease of the glass transition temperature with increasing sfMA content found by DSC technique. In addition to the α relaxation the local β relaxation of PMMA was followed and found to be accelerated in copolymers. Two relaxations related to motions of sf side chains were followed in the copolymers; a secondary relaxation attributed to motion of the side chain tail group observed for all the copolymers, γ_{sf}, and a relaxation related to the motion of sf side chains when they form a separate phase in copolymers where the side chains are self organized in ordered layers, β_{sf}.

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