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Conformational Order in Molten Amorphous Poly(ethyl methacrylate)

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Heating an amorphous polymer above its glass transition yields an isotropic melt.[1] Exceptions are liquid crystalline polymers with mesogenic groups[2] or semicrystalline polymers that exhibit conformationally disordered mesophases.[3] In such mesophases the chain dynamics are anisotropic. Rotations about the long axis, which is preferably aligned along the director of the mesophase, are much faster and larger in amplitude than fluctuations of the chain axis itself. In fact, a related situation may be considered in amorphous polymers with residual conformational order. There the chain motion in the molten state might also be anisotropic, such that rotations about the axis of an extended region of the chain occur significantly faster than reorientations of the chain axis itself. Thus, contrary to a liquid mesophase, the melt is overall isotropic, yet locally the chain dynamics are not. Clearly such anisotropic chain dynamics will have pronounced effects on the rheology of such a melt and its response to external forces.[4,5] In this paper we report the observation of such highly anisotropic chain motion in molten polymethacrylates by ^{13}C solid-state NMR spectroscopy.

Most of the measurements were performed on poly(ethyl methacrylate) (PEMA) which was 20% ^{13}C enriched at the carboxyl carbon position. It had a molecular weight $M_w = 120\,000$ and $M_w/M_n = 2.2$ as determined by GPC. Its stereoregularity was checked by ^1H NMR at 300 MHz in a $CDCl_3$ solution showing that 11% of triads are isotactic (mm), 58% syndiotactic (rr), and 31% heterotactic (rm). Due to the partial stereoregularity of the methacrylates, crystallization might occur. This was excluded by wide-angle X-ray scattering. The glass transition temperature measured by DSC was 338 K. A full description of the sample synthesis as well as a multidimensional NMR study will be published elsewhere.[6] The ^{13}C NMR experiments were carried out at 125.76 MHz with a commercial Bruker ASX-500 spectrometer in a variable-temperature double-resonance probe. Line shapes were obtained with a standard cross-polarization pulse sequence,[7] applying a contact time of 2 ms and a ^1H 90° pulse of 4.5 μs. Stimulated echoes were recorded with a $90°-t_1-90°-t_m-90°-t_1$-acquisition pulse sequence used in two-dimensional exchange experiments,[8,9] where t_1 and t_m are the evolution time and the mixing time, respectively. All chemical shifts are given relative to TMS with an uncertainty of ±1.5 ppm.

Figure 1 shows the ^{13}C NMR static spectra of the carboxyl carbon in PEMA as a function of temperature. Only the carboxyl region is plotted, which does not overlap with the signals of the aliphatic carbons. The spectrum recorded at 295 K, i.e., in the glassy state, clearly exhibits terminating edges and a peak corresponding to the three principal values of the asymmetric chemical shift tensor (CST) ($\sigma_{11} = 268$ ppm, $\sigma_{22} = 150$ ppm, $\sigma_{33} = 113$ ppm). As the temperature is raised above T_g, pronounced line-shape changes are observed, indicating large-amplitude motions with rates exceeding the width of the powder spectrum, i.e., above 20 kHz. This is consistent with the rates determined for the chain motion by dielectric and dynamic mechanical measurements[10] as well as photon correlation spectroscopy[11,12] which place the dynamic T_g for 10 kHz at 380 K. Thus the motionally narrowed spectra all correspond to PEMA in the molten state. From the line shape at 395 K (T_g + 57 K) one can clearly identify an axially symmetric CST with a noticeable peak $\bar{\sigma}_\perp = 197$ ppm and an edge at $\bar{\sigma}_\parallel = 136$ ppm. Thus, the motion of the carboxyl group is highly anisotropic, yet uniaxial. It should be noted that similar averaging effects are observed in anisotropic liquids[13] or mesophases of disordered polymers.[3] The width of the line shape then directly reflects the order parameter of the chain. Further heating results in a decrease of the width of the line shape corresponding to an axially symmetric CST, finally leading at about 435 K, i.e., 97 K above T_g, to a single peak at the isotropic chemical shift, $\sigma_{iso} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$. This behavior differs significantly from that of other amorphous polymers above T_g exhibiting isotropic motion over the full range of rates from 10^{-2} to 10^{10} Hz.[14,15]

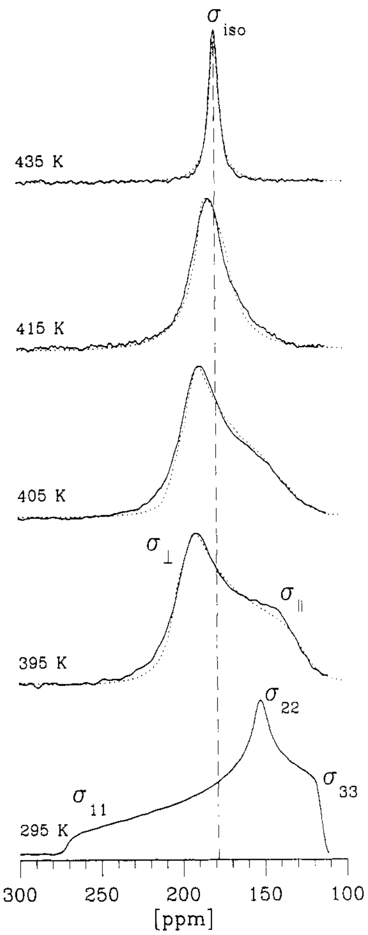

Figure 1. Experimental and simulated ^{13}C NMR spectra of the carboxyl carbon in PEMA as a function of temperature. Solid lines: experiments. Dotted lines: simulations.

In order to distinguish whether the anisotropic dynamics displayed by the carboxyl group reflects a side-group motion or indicates anisotropic chain motion, the orientation of the principal axes of the CST relative to the chain axis has to be known. In earlier measurements of the ^{13}C CST of the carboxyl carbon in the ester group[16] the most shielded component of the shift tensor (σ_{33}) was found to be perpendicular to the COO^- plane. This assignment

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has recently been confirmed in an investigation of oriented poly(methyl methacrylate) (PMMA).[17] Moreover, these experiments showed that σ_{33} is parallel to the local chain axis which is aligned along the draw direction.

Remarkably, in the motionally narrowed CST σ_{33} is only slightly affected, whereas σ_{11} and σ_{22} are averaged to yield $\sigma_\perp$. This may directly be deduced from the spectra shown in Figure 1 and is proved by detailed multidimensional NMR experiments to be published shortly.[6] From these it is concluded that in PEMA in the glass transition region coupled motion of the side group and the main chain takes place. Rocking of the backbone about its local chain axis allows the σ_{33} direction of the CST to remain essentially parallel to this axis. This motion is coupled to fast π-flips of the side group. We note that π-flips leave the σ_{33} frequency unchanged due to the second-order tensorial nature of the chemical shift interaction.[18] Thus we conclude that the anisotropic motion detected here through the carboxyl carbon in PEMA at a temperature above the dynamic glass transition temperature indicates anisotropic chain dynamics, vide infra. In the idealized case where the chain rotates as a rigid body and the σ_{33} axis is parallel to the rotation axis, a tensor with $\bar{\sigma}_\parallel = \sigma_{33}$ and $\bar{\sigma}_\perp = 0.5(\sigma_{11} + \sigma_{22})$ should result. However, even at the lowest temperature (395 K) this is not the case, presumably due to an additional conformational disorder of the chain. Further elevation of temperature decreases the conformational order and reduces the anisotropy of the averaged CST which eventually leads to the isotropic peak at 435 K.

We note that such an anisotropic motion above T_g is not observed for side groups in other amorphous polymers, for example, in polystyrene (PS)[19] and poly(vinyl acetate) (PVAc).[20] In the glassy state of the former, phenyl side-group motion (π-flips) in deuterated PS-d_5 was found. However, the ^{2}H spectra of chain and phenyl group deuterated PS are similar above T_g.[19] This clearly excludes that the phenyl rings may undergo fast rotational motions about their axes perpendicular to an essentially rigid backbone. In PVAc the motion of the carboxyl carbon in the side group was used as a probe for chain reorientation. Multidimensional ^{13}C NMR spectra[20,21] exhibited diffusive behavior due to isotropic diffusion characteristics of the backbone motion observed also in 2D exchange ^{2}H spectra of other polymers above T_g.[14,15]

However, incomplete motional narrowing has been observed before for the chain motion in the noncrystalline regions of semicrystalline polymers, i.e., polyethylene[19,22] or polyamides.[23] There, a motional model was derived which postulates the existence of long-lived topological constraints[19,22] for the chain motion resulting from the presence of crystallites or hydrogen-bonded sheets. In analogy we propose that the conformational order of PEMA has a much longer lifetime than the rapid uniaxial dynamics around the extended portions of the chain above T_g. In order to prove this conjecture experimentally at 395 K, we have used the stimulated echo sequence, which can detect ultraslow changes in the anisotropy of the CST resulting from a finite lifetime of the motional constraints.[22] Figure 2 shows stimulated echo spectra recorded for t_1 = 100 μs and with t_m equal to 1 and 2 ms. The spectra were obtained by Fourier transformation starting at the echo maximum.[22] The change of the line shapes as compared with the CP spectrum is insignificant. However, the loss of overall intensity is considerable. We note that it was possible to observe a signal of the carboxyl CST even for t_m = 20 ms. Due to the poor signal-to-noise ratio, spectra for longer t_m are not shown. The ability to detect the stimulated echo directly proves the existence of long-lived constraints on the time scale of a millisecond. The decay of the echo intensity is nonexponential, consistent with a distribution of correlation times.

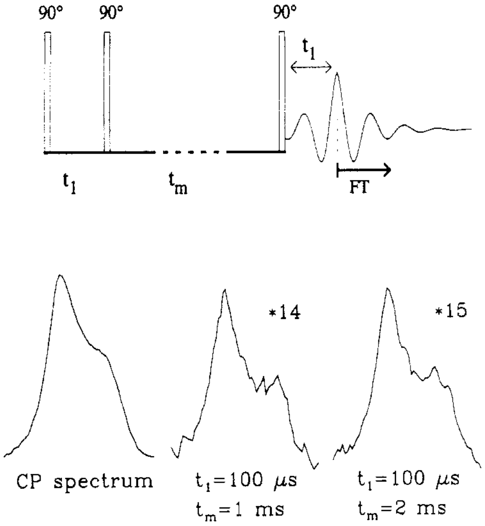

Figure 2. Upper part: Schematic pulse sequence for recording stimulated echo. The spectrum is obtained by Fourier transformation starting at the echo maximum. Lower part: Stimulated echo spectra of PEMA at 395 K obtained for evolution time t_1 = 100 μs with mixing times t_m = 1 and 2 ms. A CP spectrum is shown for comparison. The gain of the stimulated echo spectra is increased by a factor of 14 (t_m = 1 ms) and 15 (t_m = 2 ms).

Thus, the chain motion is highly anisotropic above T_g. At 395 K the rotations about the local chain axis are faster by at least 2 orders of magnitude than rotations of the chain axis itself. For such an anisotropic motion one may define a dynamic order parameter similar to the description of orientational order in liquid crystalline phases.[2,5,13] Over a considerable temperature range z_k, the σ_{33} axis (perpendicular to the COO$^-$ plane) on a time scale above 10^{-4} s displays a finite order parameter:

$$\langle P_2\rangle = \frac{1}{2}\langle[3\cos^2(z_k,Z) - 1)]\rangle \qquad (1)$$

where Z denotes the direction of the extended portion of the polymer chain to which a given COO$^-$ group belongs. This order is easily extracted from ^{13}C NMR line shape (Figure 1) according to

$$\langle P_2\rangle = \frac{\bar{\sigma}_\parallel - \sigma_{\mathrm{iso}}}{\sigma_{33} - \sigma_{\mathrm{iso}}} \qquad (2)$$

Therefore, at each temperature the experimental NMR spectrum was fitted with an axially symmetric CST, dotted line in Figure 1, yielding $\bar{\sigma}_\parallel$ as a function of temperature. The result is displayed in Figure 3 where $\langle P_2\rangle$ is plotted versus a reduced temperature $T^* = T/T_g$.

We note that the order parameter $\langle P_2\rangle$ gradually decreases from the remarkably high starting value of 0.7 to zero. No discontinuity is observed that would indicate a phase transition characteristic of a mesophase.[24] It should also be noted that here we consider only $\bar{\sigma}_\parallel$ and the local axis. The overall chain dynamics also involves the rapid uniaxial reorientation about this axis, causing substantial motional narrowing of the NMR spectrum at 395 K as compared to 295 K.

It is highly remarkable that the maximum order parameter close to T_g, which will also be present in the frozen glassy state, is as high as that in well-ordered liquid crystalline phases. Thus the conformational order of PEMA is substantial. We note again that we deal with a dynamic phenomenon. The NMR experiments prove that the chain dynamics on a time scale characteristic of the

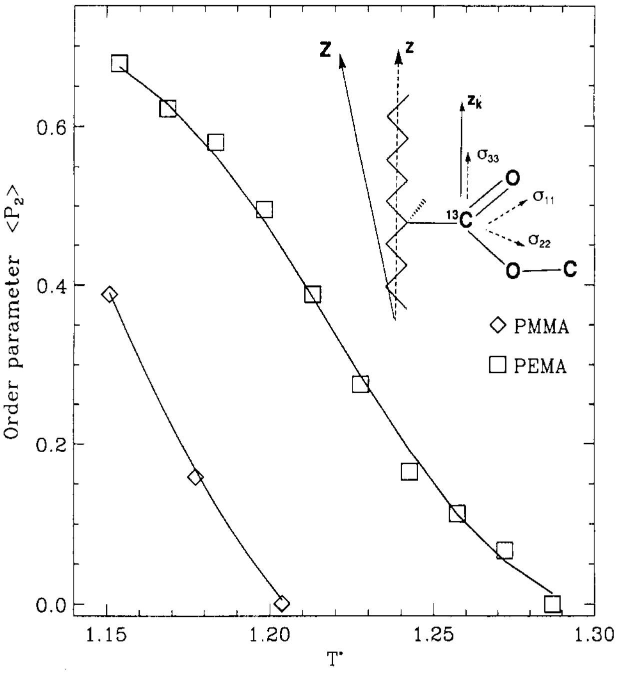

Figure 3. Temperature dependence of the order parameter $\langle P_2 \rangle = (\sigma_{\|} - \sigma_{\mathrm{iso}})/(\sigma_{33} - \sigma_{\mathrm{iso}})$ in molten PEMA (□) and PMMA (◇, T_g = 378 K). $T^* = T/T_g$; T^* = reduced temperature; T = measuring temperature; T_g = glass transition temperature. Inset: Relation between the different axes important for the description of the molecular order in PEMA and PMMA. The direction of the extended polymer chain is denoted by Z, the local chain axis by z, and the σ_{33} axis of the CST of the carboxyl carbon by z_k. Note that z and z_k are parallel.

α-process (WLF behavior) is anisotropic. Indeed, the chain motion becomes isotropic, however, on a much longer time scale (see above).

We conclude that the decrease of $\langle P_2 \rangle$ as the temperature is raised reflects decreasing conformational order. Presumably due to shortening of the extended portions of the polymer chain. Of course, one would like to relate the order parameter detected here with the structure of the polymethacrylates. Therefore, similar experiments were performed on poly(methyl methacrylate) (PMMA) revealing that PMMA also exhibits conformational order in the molten state. However, the order parameter is much lower than that in PEMA (cf. Figure 3) and the temperature range where this order exists is much smaller. Our results are also consistent with early ^{2}H-NMR data on the chain motion in PMMA[26] indicating incomplete motional narrowing at a reduced temperature T^* = 1.13. Remarkably, in a recent NMR study[17] of the orientational distribution in cold-drawn PMMA, also probed by the carboxyl carbon, a value of $\langle P_2 \rangle$ = 0.35 was determined for the maximum static order parameter of fully aligned disordered chains.[27] Thus the anisotropy of the chain dynamics slightly above T_g almost matches the maximum chain order in the glassy state. Likewise, by multidimensional NMR the chain dynamics in PMMA was also found to be anisotropic.[25] Thus PMMA also exhibits residual conformational order above T_g, however, significantly lower than PEMA.

The comparison of the two polymers suggests that in addition to the partial stereoregularity the incompatibility between the methacrylate main chain and the aliphatic side groups[28] plays an important role and causes the conformational order to be higher in PEMA than in PMMA. Indeed, we note that a similar behavior is observed in polysiloxanes, where poly(ethylsiloxane)[29] even exhibits a mesophase, whereas poly(methylsiloxane) does not.[30] It should also be noted that X-ray scattering studies of polymethacrylates[31,32] have shown anomalous behavior indicating a notable degree of packing regularity in these polymers. This behavior, likewise, could be correlated with the length of the alkyl side groups.

In conclusion we have observed highly anisotropic chain motion in amorphous PEMA well above its glass transition temperature. This reflects substantial local conformational order which is also present in other polymethacrylates and should be taken into account when considering their unusual mechanical behavior.[10]

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References and Notes

(1) See, e.g.: Sperling, L. H. *Introduction to Physical Polymer Science*; Wiley: New York, 1992.
(2) *Liquid Crystallinity in Polymers: Principles and Fundamental Properties*; Cifferi, A., Ed.; VCH Publishers: Weinheim, Germany, 1991.
(3) Wunderlich, B.; Grebowicz, J. *Adv. Polym. Sci.* **1984**, *60/61*, 1.
(4) Blinov, L. M. *Electro-optical and magneto-optical properties of liquid crystals*; Wiley: New York, 1983; Chapter 3.
(5) *Polymer Liquid Crystals*; Ciferri, A., Krigbaum, W. R., Meyer, R. B., Eds.; Academic Press: New York, 1982.
(6) Kulik, A. S.; Beckham, H. W.; Schmidt-Rohr, K.; Radloff, D.; Pawelzik, U.; Boeffel, C.; Spiess, H. W., submitted to *Macromolecules*.
(7) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.
(8) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon: Oxford, U.K., 1987.
(9) Hagemeyer, A.; Schmidt-Rohr, K.; Spiess, H. W. *Adv. Magn. Reson.* **1989**, *13*, 85.
(10) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Wiley: London, 1967.
(11) Patterson, G. D.; Stevens, J. R.; Lindsay, C. P. *J. Macromol. Sci., Phys.* **1980**, *18*, 641.
(12) Fytas, G.; Patkowsky, A.; Meier, G.; Dorfmüller, Th. *J. Chem. Phys.* **1984**, *80*, 2214.
(13) Vergoten, G.; de Jeu, W. H. *Thermotropic Liquid Crystals, Fundamentals*; Springer: Berlin, 1988.
(14) Schaefer, D.; Spiess, H. W.; Suter, U. W.; Fleming, W. W. *Macromolecules* **1990**, *23*, 3431.
(15) Pschorn, U.; Rössler, E.; Sillescu, H.; Kaufmann, S.; Schaefer, D.; Spiess, H. W. *Macromolecules* **1991**, *24*, 398.
(16) Pines, A.; Abrahamson, E. *J. Chem. Phys.* **1974**, *60*, 5130.
(17) Kulik, A. S.; Spiess, H. W. *Makromol. Chem.*, in press.
(18) Mehring, M. *High Resolution NMR in Solids*; Springer: Berlin, 1983.
(19) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193.
(20) Schmidt-Rohr, K.; Spiess, H. W. *Phys. Rev. Lett.* **1991**, *66*, 3020.
(21) Schmidt-Rohr, K.; Spiess, H. W. *Multi-dimensional NMR and Polymers*; Academic Press: New York, 1994.
(22) Hentschel, D.; Sillescu, H.; Spiess, H. W. *Macromolecules* **1981**, *14*, 1605.
(23) Miura, H.; Hirshinger, J.; English, A. D. *Macromolecules* **1990**, *23*, 2169.
(24) Finkelmann, H.; Rehage, G. *Adv. Polym. Sci.* **1984**, *60/61*, 99.
(25) Schmidt-Rohr, K.; Kulik, A. S.; Beckham, H. W.; Ohlemacher, A.; Pawelzik, U.; Boeffel, C.; Spiess, H. W., submitted for publication in *Macromolecules*.
(26) Vega, A. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1981**, *22, No. 2*, 282.
(27) *Structure and Properties of Oriented Polymers*; Ward, I. M., Ed.; Applied Science: London, 1975.
(28) Vacatello, F.; Flory, P. J. *Macromolecules* **1986**, *19*, 415.
(29) Beatty, C. L.; Pochman, J. M.; Froix, M. F.; Hinmann, D. D. *Macromolecules* **1975**, *8*, 547.
(30) Friedrich, J.; Rabolt, J. F. *Macromolecules* **1987**, *20*, 1975.
(31) Miller, R. L.; Boyer, R. F.; Heijboer, J. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 2021.
(32) Miller, R. L.; Boyer, R. F. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 2043.