Slow Ester Side-Group Flips in Glassy Poly(alkyl methacrylate)s Characterized by Centerband-Only Detection of Exchange Nuclear Magnetic Resonance

T. J. BONAGAMBA,1–3 F. BECKER-GUEDES,1,2 E. R. DeAZEVEDO,1,2 K. SCHMIDT-ROHR1,3

1Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts
2Instituto de Fıísica de Sáo Carlos, Universidade de Sáo Paulo, Sáo Carlos, Sáo Paulo, Brazil
3Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa

Received 2 May 2001; revised 23 July 2001; accepted 23 July 2001

Published online 00 Month 2001; DOI 10.1002/polb.0000

ABSTRACT: Slow side-group dynamics in a series of five poly(alkyl methacrylate)s with various side-group sizes [poly(methacrylic acid) (PMAA), poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), poly(isobutyl methacrylate) (PiBMA), and poly(cyclohexyl methacrylate), with −H, −CH3, −CH2CH3, −CH2CH(CH3)2, and −cyclohexyl alkyl substituents (CODEX), respectively] were studied quantitatively by centerband-only detection of exchange nuclear magnetic resonance (NMR). Flips and small-angle motions of the ester groups associated with the \( \beta \) relaxation were observed distinctly in the CODEX NMR data, and the fraction of slowly flipping groups was measured with a precision of 3%. In PMMA, 34% of the side groups flipped on a 1-s timescale, whereas the fraction was 31% in PEMA at 25 °C. Even the large isobutyl ether and cyclohexylester side groups flipped in the glassy state, although the flipping fraction was reduced to 22 and about 10%, respectively. In PMAA, no slow side-group flips were detected on the 1-s timescale. A striking difference in the temperature dependence of the flipping fraction in PMMA versus PEMA and PiBMA was observed. In PMMA, the flipping fraction was temperature-independent between 25 and 80 °C, whereas in PEMA, it increased continuously from 31 to 60% between 25 and 60 °C. A similar doubling was also observed in PiBMA. © 2001 John Wiley & Sons, Inc. J Polym Sci Part B: Polym Phys 39: 2444–2453, 2001

Keywords: exchange NMR; segmental dynamics; \( \beta \) relaxation; glassy polymers; inhomogeneities; local motions

INTRODUCTION

Poly(alkyl methacrylate)s are an important class of glassy polymers. Their mechanical and dielectric properties are strongly affected by the \( \beta \)-relaxation process, which is often considered an archetype of local relaxations in glassy polymers.1 In agreement with many earlier dielectric and dynamic mechanical relaxation studies,1–4 detailed multidimensional nuclear magnetic resonance (NMR) investigations of isotopically labeled poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylate) (PEMA) have shown that the \( \beta \) relaxation involves both 180° side-group flips and small-to-medium-amplitude motions around the local backbone axis.5,6 The NMR experiments have revealed that only a fraction of
the side groups are flipping, estimated to be about one-half in PMMA.\(^5\)

Recently, we introduced a new exchange NMR technique, centerband-only detection of exchange (CODEX), that enables detailed and quantitative studies of slow (0.1/s to 3000/s) motions in complex polymers, even without isotopic labeling.\(^7,8\) The fraction of slowly rotating groups, the amplitudes of motion, including slow small-amplitude oscillations, and the correlation function and correlation time of the motion can be determined with good accuracy for each site in the repeat unit. This information content exceeds that of most existing techniques. Dielectric relaxation, for instance, usually cannot distinguish whether a reduction in the dielectric loss peak after a decrease in temperature or an increase in side-group size is due to smaller-amplitude motions or a smaller fraction of mobile segments.\(^1\)

In this article, we present CODEX NMR measurements of the side-group and backbone dynamics in poly(alkyl methacrylate)s as a function of side-group size and temperature. The detection of large flipping side groups and a different temperature dependence of the flipping fraction in PMMA is particularly noteworthy.

**EXPERIMENTAL**

**Materials**

Several glassy poly(alkyl methacrylate)s (PRMAs) were studied. Isotactic and atactic poly(methyl methacrylate)s (iPMMA and aPMMA, respectively), PEMA, poly(isobutyl methacrylate) (PiBMA), and poly(cyclohexyl methacrylate) (PcHMA) were purchased from Scientific Polymer Products, Inc. The \(^{13}\)C-labeled PEMA sample has been described elsewhere.\(^6\) Poly(methacrylic acid) (PMAA) from Scientific Polymer Products was also studied. All samples were melt-compressed into a cylinder fitting snugly into the NMR rotor, except PMAA, which was compressed into the rotor in the form of the original fine powder. iPMMA was melt-compressed and quenched in liquid nitrogen a few hours before the experiment so that it could be measured in the amorphous phase.

Table I summarizes the molecular weights (MWs) and glass-transition temperatures (\(T_g\)'s) of all poly(alkyl methacrylate)s studied in this work.

**NMR**

The CODEX NMR experiments were performed at 75 MHz for \(^{13}\)C on a Bruker DSX-300 NMR spectrometer. Data were acquired in both 4-mm and 7-mm double-resonance variable-temperature magic-angle spinning probe heads, with \(^{13}\)C and \(^1\)H 90° pulse lengths of about 3.5 ms and \(^1\)H decoupling at \(gB_1/2\pi = 80\) kHz at spinning rates ranging from 3.5 to 10.0 kHz. The recycle delay used for almost all the samples was 1.5 s; for PMAA, it was 2 s. The cross-polarization time was 1.5 ms for all samples. The typical measuring time per pure-exchange CODEX spectrum was around 2.0 h. To eliminate effects of spectrometer drift, we alternated measurements between the CODEX and reference signal approximately every 2 min. The total number of scans for each spectrum acquired ranged from 1280 to 2560, depending on the sample.

**CODEX NMR Method**

The pulse sequence for the CODEX NMR experiment is shown in Figure 1. The principle of the experiment is briefly summarized here. A more detailed discussion can be found in refs. 7 and 8. Basically, the experiment detects the signal reduction due to dephasing of magnetization resulting from changes in the orientation-dependent chemical-shift frequencies that occur because of...
segmental reorientations during the long mixing time \( t_m \). For \( N/2 \) rotation periods, the spins evolve under the anisotropic chemical shift, which is recoupled\(^7\)-\(^9\) by two 180° pulses per rotation period \( t_r \) in a spinning-speed-independent fashion. Then, the magnetization is stored along the z direction so that it does not precess or dephase during long \( t_m \), which is an integer multiple of \( t_r \). If no motions occur during \( t_m \), the chemical-shift evolution, after a readout pulse and another \( N/2 \) rotation periods under the recoupled chemical-shift anisotropy (CSA; total time of \( Nt_r \)), is refocused at the start of detection. If segmental reorientation does occur during \( t_m \), the orientation-dependent frequency has changed, and the CSA is not completely refocused. The resulting dephasing is observed with high sensitivity as a decrease in the detected line intensity. For the removal of the effects of \( T_1 \) relaxation during \( t_m \) and of \( T_2 \) relaxation during \( Nt_r \), a reference spectrum \( S_0 = S(0, \delta Nt_r) \) is measured that has all the same relaxation factors but no motion during \( t_m \). It is obtained by the simple interchanging of the durations of \( t_m \) and \( t_r \).\(^8\) For the standard quantitative analysis, the CODEX intensity \( S = S(t_m, Nt_r) \) is subtracted from that of the reference spectrum \( S_0 = S(0, Nt_r) \) to obtain the pure-exchange intensity \( \Delta S = S_0 - S \). An example of a set of spectra \( S_0, S \), and \( \Delta S \) is shown in Figure 2. The difference signal intensity \( \Delta S \) of the COO resonance is plotted after normalization by division by \( S_0 \).

High spinning rates \( (v_r) \) can be used to obtain virtually sideband-free spectra because the dephasing is only a function of the total time \( Nt_r \).\(^8\) If we combine measurements at different spinning speeds, the exchange intensity \( \Delta S/S_0 \) can be measured for almost any desired time \( Nt_r \), rather than only in integer increments of a specific \( t_r \). Only very short times are difficult to reach because they require very high spinning rates \( (v_r = 1/t_r) \). To suppress spinning sidebands during detection, we can use the total suppression of sidebands sequence\(^8,10\) before detection.

The \( t_m \) dependence of the pure-exchange CODEX intensity yields the correlation functions of the dynamics on a millisecond to second timescale, with the correlation time as a time constant.\(^7\)

**Motional Amplitude**

The amplitude of the reorientations during \( t_m \) can be determined through variation of the duration \( Nt_r \) of the evolution under the recoupled CSA. The smaller the reorientation angle is, the slower the increase is of the normalized exchange intensity \( \Delta S/S_0 \) with \( Nt_r \).\(^8\) Figure 3(b) shows simulated curves for rotations by a small angle \( \alpha \) around the local chain axis, which coincides with the normal of the ester side group [Fig. 3(a)]. The curves reveal good resolution for small reorientation angles, which can be explained by an analysis in terms of the CSA difference tensor.\(^8\) The chemical-shift tensor orientation used in the simulations has been taken from ref. 5.

However, flips by \( \gamma = 180^\circ \) around the C—C bond connecting the side group to the backbone lead to large frequency changes and faster dephasing, as also shown in Figure 3(b). Identical frequency changes would result from rotations around the ester plane normal by \( \alpha = 54^\circ \) because the \( a_{11} \) principal axis of the CSA tensor makes an angle of \( 54^\circ/2 \) with the C—C bond to the backbone [Fig. 3(b)].

Figure 3(c) shows how the experimentally observed bimodal CODEX curve of PEMA COO side...
groups can be decomposed into a 180° flip fraction and a small-amplitude component. In the fit, a single value of $\alpha = 6^\circ$ was used. Realistically, a distribution of $\alpha$ angles is to be expected; the fits of the experimental data discussed later use such distributions.

**Mobile Fraction from CODEX Data**

Information about the fraction of mobile segments ($f_m$) is obtained from the long-time exchange intensity ($E_\infty$), which also depends on the number ($M$) of equivalent orientational sites accessible in the motional process. For instance, for 180° side-group flips, $M = 2$. Because a fraction of at least $1/M$ of the mobile species will always be found in the originally selected site, we obtain a long-time exchange intensity of

$$E_\infty = \Delta S/S_0 \sim \tau_c/N_{t_r}$$

where $\Delta$ is the CSA parameter. For the side-group flips in PRMAs, $M = 25.8$; therefore, eq 1 yields

$$f_m = 2E_\infty$$

Thus, the flipping fraction is twice the level of the intermediate plateau seen, for instance, in Figure 3(c) before the onset of the small-angle contribution. For diffusive reorientations, $M \gg 1$, and if all segments participate in the rotational-diffusion process, $E_\infty \sim 1$ will be reached at very long times.11

**RESULTS**

For three different PRMAs, Figure 4 shows the exchange intensity due to side groups that have reoriented during $t_m$. For each polymer, curves for various recoupling times $N_{t_r}$ are displayed. When this time is shorter than 1000 $\mu$s, the small-angle motions do not contribute significantly to the exchange intensity. This is confirmed by the good agreement of the curves for $N_{t_r} < 1000 \mu$s, whereas at $N_{t_r} > 2000 \mu$s [see Fig. 4(a,d)], the small frequency changes arising from slow small-amplitude motions have had time to generate significant dephasing and a resulting significant increase in the exchange intensity $\Delta S/S_0$. A detailed analysis of the $N_{t_r}$ dependence in Figure 3 and later in the text confirms this.
The data in Figure 4(a,b) for aPMMA and PEMA, respectively, were taken between 6 and 30 °C. In this temperature range, no significant change is observed in the plateau values $E'_\alpha$ of the curves; these are of the most interest in this work because they reveal the flipping fractions $f_m$ according to eq 2. The initial rise measured in Figure 4(a) is slightly slower at lower temperatures, as expected for the thermally activated $\beta$ relaxation. In Figure 4(c), data for $^{13}$C-labeled PEMA show an initial slope similar to the slope for the unlabeled PEMA in Figure 4(b), but at $t_m > 100$ ms, they start to deviate, continuing to increase. This can be attributed to exchange by $^{13}$C spin diffusion, generated by the homonuclear dipolar couplings between the $^{13}$C spins. Because of the $^{13}$C enrichment, the average distance between $^{13}$COO groups is decreased and the dipolar coupling is increased, and as a result, the spin-exchange process is much more efficient than for the unlabeled samples.

For PCHMA [Fig. 4(d)], the plateau, that is, the fraction of flipping side groups, is significantly lower than that for PMMA and PEMA. However, the clear rise of the exchange intensity with $t_m$ in Figure 4(d) to a nearly fixed long-term plateau shows unambiguously that about 10% of the large cyclohexyl side groups still flip on the 1-s timescale. To ensure that only flips are detected, we took the data with a short recoupling time $N_{t_r}$ where only large-amplitude reorientations produced significant exchange intensity. Note that spin diffusion can be excluded because it would have resulted in a continuing increase of the exchange intensity with $t_m$. The additional exchange intensity at longer times, $N_{t_r} = 2182$ $\mu$s,
Effect of Side-Group Size on Side-Group Motion

The variation of the $t_m$ dependence of the exchange intensity in Figure 4 with $Nt_r$ suggests that side-group motions of both large and small amplitudes occur. This is confirmed by the recording of the exchange intensity as a function of $Nt_r$ at a fixed $t_m = 500$ ms (100 ms for the $^{13}$C-enriched PEMA, where spin diffusion must be avoided). The resulting data in Figure 5 show bimodal curves for all PRMAs. As discussed in the text, the bimodal behavior observed is due to flips of some side groups and small-angle motions of others.

Figure 5. Motional-amplitude-dependent CODEX curves as a function of the recoupling time $Nt_r$: data for (a) aPMMA and iPMMA, (b) unlabeled PEMA (open symbols) and $^{13}$COO-labeled PEMA (filled symbols), (c) PiBMA, (d) PcHMA (the initial rise is due to about 10% of the flipping side groups), and (e) PMAA (here, no slow-flipping fraction is detected). The mixing time was 500 ms, except for $^{13}$COO-PEMA ($t_m = 100$ ms), (f) compilation of the fit curves for the six materials in Figure 5(a–e). The bimodal behavior observed is due to flips of some side groups and small-angle motions of others (see the text).
context of Figure 3, the fast initial rise can be safely attributed to the 180° flips detected previously in 13C-labeled PMMA and PEMA by two-dimensional exchange NMR.5,6 The slower second increase arises from slow small-angle motions, whose exact nature is difficult to determine by CODEX alone.

At ambient temperature, the flipping fraction is largest, 34%, in aPMMA [Fig. 5(a)]. In amorphous iPMMA, the flipping fraction is slightly lower, 27%. This indicates that the flipping fraction in the racemo (syndiotactic) dyads of PMMA is slightly higher (38%) than in the meso (isotactic) dyads. However, overall it must be concluded that a similar fraction of side groups flip in both the meso and racemo dyads of PMMA.

In PEMA and PiBMA, 31 and 22%, respectively, of side groups flip on the 1-s timescale [Fig. 5(b,c)]. The step from the 180° flips in the curve from PcHMA [Fig. 5(d)] is small but clearly detectable. Together with the mixing-time-dependent data of Figure 4(d), this shows unambiguously that about 10% of the large cyclohexyl side groups flip on the 1-s timescale. Spin diffusion cannot account for the first step in the data. This is proven conclusively by the plateau at long \( t_m \) in the data of Figure 4(d); spin diffusion would result in a continuous rise with \( t_m \), as in Figure 4(c).

No flipping side groups (<5%) are detected in PMAA on the 1-s timescale [Fig. 5(e)]. According to ref. 12, a COOH group is sufficiently asymmetric to avoid having the \( \sigma_{11} \) principal axis of the CSA tensor along the C—C axis (which would make the 180° flip invisible in the NMR experiment). Therefore, it seems unlikely that slow 180° flips of the COOH groups occur. Rather, it must be concluded that the flips are either very fast, so that the experiment detects only an invariant average frequency, or, more likely, that they are very slow or completely suppressed, presumably by H bonding between COOH groups.

The fit curves for the six samples studied are combined in Figure 5(f). The small-amplitude components were fit by two components. The first is a \( \sigma = 6° \) Gaussian distribution in the \( \alpha \) angle [see Fig. 3(a,b)] with a weight equal to half the flipping fraction as given previously for each sample. This component is assigned to even numbers of flips, which return the side group approximately, but not exactly, to its original orientation. The second component is a \( \sigma = 3.5° \) Gaussian fraction of varying weight, which is ascribed to the millisecond small-amplitude motions of side groups that do not flip. It was 30% in aPMMA, 5% in iPMMA, 43 and 20% in unlabeled and labeled PEMA, 54% in PiBMA and PcHMA, and 50% in PMAA. The error bars in the experimental data indicate that the uncertainty in the weight of the 3.5° Gaussian component is about ±15%. These are not fast librations but motions on a millisecond timescale. More detailed investigations of the motional geometry of these slow side-group dynamics and the small-amplitude motions of the backbone are in progress.

Effect of Temperature on Side-Group Motion

Figure 6 shows \( N_t \)-dependent CODEX curves of PMMA, PEMA, and PiBMA for increasing temperatures. The data for PMMA in Figure 6(a) show no detectable change over a 55 K temperature range. This indicates that the mobile fraction is not just an arbitrary division in a broad distribution of correlation times but that immobile side groups of PMMA are trapped at all temperatures below \( T_g \).

In contrast, the data for PEMA [Fig. 6(b)] show a significant increase in the fraction of flipping groups above 25 °C, even though all the measurements were performed below \( T_g \), that is, in the glassy state. To confirm this unexpected increase in the flipping fraction, we measured a second PEMA sample; see Figure 6(c). It shows the same dependence of the flipping fraction on temperature. For PiBMA, the data shown in Figure 6(d) indicate a similar increase in the flipping fraction, although from a lower initial level.

In Figure 7, the fraction of flipping side groups is plotted as a function of temperature for the four samples investigated. The contrast between the constant flipping fraction in PMMA and the nearly linear increase of the flipping fraction above 25 °C in PEMA is striking.

DISCUSSION

The quantitative CODEX NMR data presented here show that in the glassy state, only a fraction of ester side groups of poly(alkyl methacrylates) undergo slow 180° flips. For instance, in PMMA only about one-third of side groups flip. Before the advent of CODEX, no technique was available to determine the flipping fraction accurately. Thus, these quantitative CODEX NMR experiments re-
veal the fraction of mobile segments as a third
fundamental aspect of β relaxations in glassy
polymers, beyond the rate and amplitude of β-re-
laxation segmental motions.

The data also show that even some of the large
isobutyl and cyclohexyl side groups can undergo
slow 180° flips at ambient temperature. It re-
 mains to be investigated whether the entire side
group flips over or whether the center of mass of
the large side group remains essentially in the
same place whereas the flip is accommodated by a
conformational change.

A surprising difference in the temperature de-
pendence of the flipping fraction in PMMA versus
PEMA and PiBMA has been discovered. The data
in Figures 6(a) and 7 show that the flipping frac-
tion (and also the small-amplitude motion) in
PMMA is temperature-independent between 25
and 80 °C, whereas a strong increase is observed
for PEMA and PiBMA. As a result, at 60 °C the
flipping fraction of the larger PEMA side groups

\[ \frac{\Delta S}{S_0} \]

\( \delta N_T \)

\( a \) 80 °C
\( \Delta \) 60 °C
\( \triangledown \) 30 °C
\( \blacklozenge \) 25 °C

\( b \) 60 °C
\( \circ \) 40 °C
\( \blacksquare \) 30 °C
\( \blacklozenge \) 25 °C
\( \blacklozenge \) 6 °C

\( c \) 80 °C
\( \Delta \) 60 °C
\( \triangledown \) 40 °C
\( \blacklozenbox \) 25 °C

\( d \) 55 °C
\( \Delta \) 25 °C

Figure 6. CODEX data showing the temperature dependence of the slow motions,
particularly the fraction of mobile side groups, in (a) PMMA, (b) unlabeled PEMA, (c)
13COO labeled PEMA, and (d) PiBMA; \( t_m = 500 \text{ ms} \), except in (c), where \( t_m = 100 \text{ ms} \).

\[ \frac{\Delta S}{S_0} \]

\( \delta N_T \)

\( a \) PMMA
\( b \) PEMA
\( c \) PEMA labeled
\( d \) PiBMA

Figure 7. Temperature dependence of the fraction of
flipping side groups in aPMMA (solid triangles), two
PEMA samples (open circles, commercial PEMA with
\( T_g = 66 \degree C \); filled squares, 13COO-labeled PEMA with
\( T_g = 81 \degree C \)), and PiBMA (open triangles).
is nearly twice as high as that of the smaller PMMA side groups.

What is the origin of this different behavior? A potential explanation is indicated in Figure 8. The side group of PMMA has fewer degrees of freedom than are available to the longer side groups of the other PRMAs. As a result, its shape asymmetry [see Fig. 8(a)] is temperature-independent, and steric inaccessibility of the conformation after a 180° flip remains unchanged. In PEMA, the side group is also strongly asymmetric in the trans–trans conformation [see Fig. 8(b)], which is the dominant conformation found at ambient temperature. However, if the C—O—C—C bond takes gauche conformations at elevated temperatures, a more symmetric side-group conformation results [see Fig. 8(c)]. This would facilitate the flips because now the CH₂ group blocks out space for the CH₃ group after the flip, and vice versa. The same symmetrization could occur by a gauche C—C—O—C bond in the isobutyl side group [see Fig. 8(d)].

The conformation-based hypothesis proposed here to explain the striking increase in the flipping fraction in PEMA could be tested experimentally by an extension of the measurements of ref. 13 to higher temperatures. However, this requires a sample of multiply ¹³C-labeled PEMA.

The absence of a temperature dependence of the flipping fraction in PMMA indicates that the flipping fraction is not an arbitrary quantity resulting from the 1-s cutoff of our experiments. If the flipping fraction were just the result of such a cutoff within a broad distribution of correlation times, the temperature increase should increase the flipping fraction, as more side groups would flip on the 1-s timescale. The temperature independence of the curves in Figures 6(a) and 7 suggests that the flipping fraction in PMMA is a fixed, structurally determined quantity.

CONCLUSIONS

Detailed and quantitative information on the slow side-group motions in five poly(alkyl methacrylate)s was obtained by CODEX NMR. Both large-amplitude side-group flips and slow small-amplitude rotations were detected. Only a fraction of side groups, 34% in PMMA, underwent the slow flips. Even large side groups flipped, but the flipping fraction was reduced (e.g., to 10% for cyclohexyl groups). Differences in the temperature dependence of the fraction of flipping side groups in PMMA and PEMA were discovered. Although the flipping fraction remained unchanged in PMMA, it rose continuously between 25 °C and T_g in PEMA and PiBMA.

Financial support by the National Science Foundation (grant DMR-9703916) is gratefully acknowledged. K. Schmidt-Rohr thanks the Arnold and Mabel Beckman Foundation for a Young Investigator Award that helped to support this work. T. J. Bonagamba, F. Becker-Guedes, and E. R. deAzevedo thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (Brazil) for fellowships. The Materials Research Science and Engineering Center at the University of Massachusetts provided partial support for the NMR facility. This work was partially supported by the Director for Energy Research, Office of Basic Energy Science, in the Materials Chemistry Program of Ames Laboratory, which is operated for the U.S. Department of Energy by Iowa State University under contract no. W-7405-Eng-82. The authors thank Professor H. W. Spiess for making the ¹³C-labeled PEMA sample available.

REFERENCES AND NOTES