



HAL
open science

Probing the cooperative dynamics varying the side-chain length of poly(alkyl acrylate)s: ESR experiments

Laura Andreozzi, Ciro Autiero, Massimo Faetti, Marco Giordano, Fabio Zulli

► To cite this version:

Laura Andreozzi, Ciro Autiero, Massimo Faetti, Marco Giordano, Fabio Zulli. Probing the cooperative dynamics varying the side-chain length of poly(alkyl acrylate)s: ESR experiments. *Philosophical Magazine*, 2007, 87 (3-5), pp.799-810. 10.1080/14786430601003858 . hal-00513777

HAL Id: hal-00513777

<https://hal.science/hal-00513777>

Submitted on 1 Sep 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Probing the cooperative dynamics varying the side-chain length of poly(alkyl acrylate)s: ESR experiments

Journal:	<i>Philosophical Magazine & Philosophical Magazine Letters</i>
Manuscript ID:	TPHM-06-Apr-0133.R1
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	12-Jul-2006
Complete List of Authors:	Andreozi, Laura; Univirsity of Pisa, Physics Autiero, Ciro; University of Pisa, Physics Faetti, Massimo; University of Pisa, Physics Giordano, Marco; University of Pisa, Physics Zulli, Fabio; University of Pisa, Physics
Keywords:	EPR, polymers
Keywords (user supplied):	cooperativity, crossover, probe dynamics



Probing the cooperative dynamics varying the side-chain length of PAAs

Probing the cooperative dynamics varying the side-chain length of poly(alkyl acrylate)s: ESR experiments

LAURA ANDREOZZI*, CIRO AUTIERO, MASSIMO FAETTI, MARCO GIORDANO, FABIO ZULLI

Department of Physics 'E. Fermi', University of Pisa and polyLab-CNR,

largo Pontecorvo 3, 56127 Pisa, Italy

The rotational dynamics of the tracer cholestane dissolved in unentangled nearly monodisperse poly(alkyl acrylate) melts has been investigated by means of electron spin resonance spectroscopy. Three samples of almost same molecular weight were selected, poly(methyl acrylate) poly(ethyl acrylate) and poly(n-butyl acrylate), whose linear viscoelastic properties were also characterised. Large temperature intervals were found with power laws relating shear flow relaxation and probe rotational diffusion. The main aim of this paper was the study of the sharp crossover between two different fractional regimes that for all the samples was observed at a temperature $T_C=1.15-1.25T_g$. The decoupling from structural relaxation at $T < T_C$ was ascribed to the onset of cooperative effects on the length scale probed by the tracer. These results fit in the general scenario regarding the dynamical information extractable from ESR on cholestane, a probe with its long axis dimension greater than the typical length characterising the rigid segment of polymers.

Keywords: Cooperativity; Crossover; Polymers; Side-chain; Probe dynamics; ESR

* Author for correspondence. E-mail: laura.andreozzi@df.unipi.it.

Probing the cooperative dynamics varying the side-chain length of PAAs

1. Introduction

The comprehension of the mechanisms of relaxation in glass-forming materials in their supercooled state is an important still unresolved topic in condensed matter physics [1, 2]. The temperature scaling of relaxation times exhibits a pseudo-Arrhenius form $\tau_{\infty} \exp(E_T/kT)$ (k is the Boltzmann's constant) with a T -dependent activation energy E_T . The most widely employed Vogel-Fulcher (VF) [3] form shows an observation window in which, in many cases [4], a single set of VF parameters is not able to give account of the experimental relaxation time data, and its coefficients have to vary around a certain temperature. This suggests that the mechanism of slow structural relaxation makes some alterations there. In particular, dynamical changes take place in a narrow range of temperatures typically located at about $1.1-1.2T_g$ and have been often observed with different spectroscopies [5-7]. These phenomena have been often ascribed to the onset of cooperative molecular rearrangements, and to the effect of the dynamic heterogeneity developing on approaching the glass transition from above. When polymeric materials are considered, also polydispersity and topology could play important roles.

Several works suggested that the length scale characterising the heterogeneity and the cooperative regions is of the order of the nanometer [5,8,9]. This represents one of the reasons of the appeal exerted by molecular probe spectroscopy, as its recent application in the framework of dielectric spectroscopy also testifies [10]. With time resolved fluorescence measurements of doped malachite green molecules dissolved in different glass formers [11] and with positron annihilation lifetime spectroscopy studies [12] dynamic anomalies were enlightened in the range $1.15-1.4T_g$.

As far as the study of this crossover region is concerned, electron spin resonance spectroscopy (ESR) deserves consideration, due to its well-known sensitivity on the nanometer length scale and nanosecond time scale. ESR investigation of rotational dynamics of different paramagnetic tracers dissolved in low molecular weight glass formers and polymers evidenced the existence, in the

Probing the cooperative dynamics varying the side-chain length of PAAs

supercooled region, of a dynamic crossover at about $1.2T_g$ [13-16] and of partial coupling between probe rotation and shear viscosity [14-17].

In this work, we present ESR results on the temperature dependence of the rotation of the cholestane spin-probe dissolved in narrow distribution poly(alkyl acrylate) (PAA) samples of very comparable molar weight: a poly(methyl acrylate) (PMA), a poly(ethyl acrylate) (PEA), and a poly(*n*-butyl acrylate) (PnBA). The main aim of this work was to enlighten the influence of the side chain length on the dynamic anomalies observed in the crossover region. A linear viscoelastic characterisation of the samples is also presented.

2. Materials and experimental details

The molecular structure of the repeating unit of the PAAs differs in the number n of the CH₂ groups along the alkylic side-chain (figure 1a). The PMA ($n = 0$) and the PnBA ($n = 3$) samples were sealed by Polymer Source Inc. (Montreal, Canada), which provided molar mass data from size exclusion chromatography (SEC) using polystyrene standards. The PEA sample ($n = 1$) was synthesized as described in [16]. SEC calibrated with monodisperse polystyrene standards allowed the determination of the M_n and the M_w average masses and the polydispersity index M_w/M_n [18]. Measurements of the glass transition temperature T_g were obtained by differential calorimetric scans (Perkin Elmer DSC7). The thermograms were recorded on heating at 10 K/min after quenching at 40 K/min. Molar mass data and the T_g temperatures of the samples are given in table 1.

[Insert figure 1 about here]

[Insert table 1 about here]

Linear viscoelastic measurements on the PAA samples were carried out with a Haake RS150H rheometer by using a parallel plate system (diameter 20 mm). The gap between the plates was slightly

Probing the cooperative dynamics varying the side-chain length of PAAs

increased on increasing temperature (900-1100 μm) to account for the thermal dilatation. Iso-thermal frequency sweeps from 10^{-2} to 24.4 Hz, and creep and flow measurements were performed to gain information on the zero-shear viscosity and the dynamic moduli.

X-band ESR measurements were performed on the probe-polymer systems by means of a Bruker ER200D SRC spectrometer equipped with the Bruker BVT100 temperature control apparatus with a nominal accuracy of ± 0.1 K.

The stiff nitroxide molecule 3[beta]-doxyl-5[alpha]-cholestane (figure 1b) was used as paramagnetic probe. The samples were obtained mixing two solutions containing a predetermined amount of polymer and spin-probe. The resulting solution was evaporated to complete dryness (10^{-4} cholestane/repeating-unit molar ratio) in a standard ESR tube. Spectra in the ESR slow motion regime, close to T_g , were carefully recorded, allowing one to measure spectral distances with sensitivity of 10^{-2} gauss (via a NMR gaussmeter ER035M). The principal components of the magnetic Zeeman (\mathbf{g}) and hyperfine (\mathbf{a}) tensors [19] of the spin-probe in PAA samples were drawn by the powder ESR spectrum recorded at 140 K [20]. The components of \mathbf{g} and \mathbf{a} of cholestane, identical for the probe dissolved in the different PAAs, are reported in table 2 in the molecular frame. These values determine the response of the system through the spin Hamiltonian: $H = H_s + H_{sB} + H_B$. H_s is the Hamiltonian invariant under rotation, H_B describes the rotational degrees of freedom of the thermal bath and H_{sB} couples the spin and orbital variables. The analysis of the ESR spectra is well established [21-23]. Numerical simulations based on the generalised Mori theory allow one to extract dynamic information from the experimental line-shapes [24].

[Insert table 2 about here]

3. Results

Probing the cooperative dynamics varying the side-chain length of PAAs

Figure 2 shows the temperature dependence of the zero-shear viscosity η of the PAA samples, obtained from creep, flow and dynamic measurements. The η temperature dependence of each sample is well reproduced (figure 2) by a unique Vogel-Fulcher law [3] in the whole temperature range:

$$\eta(T) = \eta_{\infty} \exp\left(\frac{T_b}{T - T_0}\right). \quad (1)$$

The values of the prefactors η_{∞} , the pseudo-activation energies (expressed in kelvin) T_b , and the Vogel temperatures T_0 are reported in table 3.

[Insert figure 2 about here]

[Insert table 3 about here]

In the whole investigated range, from $T_g + 10$ K up to $T_g + 100$ K, the time-temperature superposition (TTS) principle was found to be applicable. The horizontal and vertical shift factors a_{Tr} and b_{Tr} at the reference temperature T_r (279 K, 270 K, and 259 K respectively for PMA, PEA, and PnBA), as well as the master curves, are obtained in this work by mathematically shifting the experimental isotherm frequency sweeps of the complex modulus $G^*(\omega)$ (figure 3).

[Insert figure 3 about here]

The PAA samples behave in a thermo-rheological simple way and the shift factors $a_{Tr}(T)$ are well described by the Williams-Landel-Ferry (WLF) law [25]:

$$\log a_{Tr}(T) = \frac{-c_1(T - T_r)}{T - T_r + c_2}. \quad (2)$$

The values of the c_1 and c_2 T_r -depending parameters, as well as the temperature invariants $c_1 c_2 \ln 10$, $T_r - c_2$, and the c_1^g and c_2^g parameters extrapolated at T_g are given in table 3. All the samples, within the experimental errors, fulfil the relationships $T_b = c_1 c_2 \ln 10$ and $T_0 = T_r - c_2$, relating VF and WLF parameters if TTS holds and in the framework of the free volume approach.

Probing the cooperative dynamics varying the side-chain length of PAAs

No evidence of rubbery plateau was found (according to the minimum $\tan\delta$ criterion), as expected for polymer masses of the order of the entanglement mass M_e [26]. In the lowest frequency region, the curves show the behaviour of monodisperse linear polymers $G' \propto \omega^2$ and $G'' \propto \omega$. The wide range of frequencies in which the moduli of PMA are quite parallel follows from the fact that the ratio between the molar and the entanglement mass for the PMA sample is higher than for the other samples.

The ESR measurements on PAAs were carried out in the temperature range from 205 K to 410 K. Because of its nearly axial symmetry, the cholestane probe exhibits an anisotropic rotational diffusion described in terms of spinning τ_{\parallel} and tumbling τ_{\perp} correlation times. For the studied temperatures, the anisotropy ratio $\tau_{\parallel}/\tau_{\perp}$ varied from 12 to 20 on cooling.

In figure 4 the temperature dependence of τ_{\parallel} is reported for all the PAA samples. Different dynamic regions can be identified, which are detailed in table 4. Figure 5 shows data for PnBA only. In each region, the correlation time is well represented assuming either the Arrhenius behaviour (regions I and IV)

$$\tau_{\parallel}(T) = \tau_{\parallel\infty} \exp\left(\frac{\Delta E}{kT}\right) \quad (3)$$

or the Vogel-Fulcher (regions II and III) one

$$\tau_{\parallel}(T) = \tau_{\parallel\infty} \exp\left(\frac{T_b}{T - T_0}\right). \quad (4)$$

The fit parameters pertinent to the different regions of the PAA samples are given in table 4.

[Insert figure 4 about here]

[Insert figure 5 about here]

[Insert table 4 about here]

4. Discussion

Probing the cooperative dynamics varying the side-chain length of PAAs

1
2
3 The discussion of region I can be found in [27], where the results of the PnBA and PEA samples were
4
5 analysed with data of other four poly(ethyl acrylate)s samples. A dependence of the onset temperature
6
7 T_A with the mass for PAAs was inferred, able to account of the lack of crossover to region I in the
8
9 investigated T -range for PMA.
10
11

12
13 An activated regime (region IV) is also found on lowering the temperature down to the glassy
14
15 state. The values of the activation energies (table 4) suggest that the rotational dynamics is coupled to
16
17 secondary relaxation processes of PAAs. In particular, for PEA and PMA, ΔE agrees with the
18
19 activation energy of secondary β relaxation found by dielectric spectroscopy and ascribed to the
20
21 dynamic of the -COOR side chain [28], while for PnBA, ΔE coincides with the activation energy of
22
23 the relaxation of the -OR group in the side-chain [29].
24
25
26

27
28 A different mechanism drives the probe rotational relaxation in the other two dynamical regions
29
30 II and III. There, the rotational diffusion is well described by VF laws characterised by the same value
31
32 of the Vogel temperature T_0 . Such a value is also coincident, within the experimental errors, with the
33
34 T_0 value found for the shear viscosity (table 3). Accordingly, the probe dynamics appears to be coupled
35
36 with the collective dynamics of the polymer that is responsible for the glass transition. For all the
37
38 investigated samples, the crossover between the two regimes takes place at a temperature T_C located in
39
40 the range $1.15-1.25T_g$ (see table 5) that well agrees with the critical temperature range of the mode
41
42 coupling theory [30], and with related recent experimental studies [7] in polymers. In this temperature
43
44 interval, crossovers between different dynamic regimes in glass-formers are also a current finding of
45
46 various spectroscopies [5, 6, 11, 12]. The above result on PAAs intrigues and proposes the ESR as a
47
48 major spectroscopy to investigate the crossover dynamics. Actually, similar dynamic anomalies, related
49
50 to the occurrence of a larger decoupling from the structural relaxation of the host matrix, were found
51
52 for the cholestane rotation in other polymers [14-16] whereas, with the smaller paramagnetic probe
53
54
55
56
57
58
59
60

Probing the cooperative dynamics varying the side-chain length of PAAs

tempo, the α - β splitting of the relaxation was observed in PVAc [13] and PPG4000 [31] at $1.2T_g$. This also suggests that different dynamical features can be observed with probe spectroscopy, by selecting proper length scales [27].

[Include table 5 about here]

For all the PAA samples the value of the spinning correlation time at T_C , $\tau(T_C)$, is of the order of magnitude of the monomeric rotational correlation time τ_m , as found from NMR measurements in polybutadiene and polyethylene-oxide solutions [32]. Interestingly enough, in this work τ_m resulted to be molecular weight independent for homologue polymer species, as found also elsewhere for $\tau(T_C)$ in PEAs [16]. Nevertheless, a weak dependence of $\tau(T_C)$ on the side-chain length can be here appreciated. The bigger the monomeric unit the slower the time, in fact $\tau(T_C)$ values ≈ 30 ns in PMA, ≈ 33 ns in PEA, and ≈ 37 ns in PnBA.

[Include figure 6 about here]

By inspection of figure 6, one can appreciate the sharpness of the dynamic crossover seen by ESR spectroscopy. It also appears that the relation between guest rotational dynamics and host viscous flow follows fractional laws:

$$\tau_{||} \propto [\eta(T)]^{\xi} \quad 0 < \xi \leq 1, \quad (5)$$

that also were found to work in other ESR studies by us [14-17], and also with other kinds of probe spectroscopy [11].

The values assumed by the exponent of equation 5 for the PAAs in the regions II and III, for sake of clarity referred to as ξ and ξ' respectively, are reported in table 5. They can be expressed as the ratio of the pseudo-activation energy of regions II or III over the one obtained from viscosity, and represent the coupling degree between probe dynamics and structural relaxation of the host [15]. The decoupling ($\xi < 1$) found in the region II has to be ascribed to steric hindrance effects of the guest-host geometry

Probing the cooperative dynamics varying the side-chain length of PAAs

and interaction [15]. This statement seems to be supported by the results in PEA polymers [16], where ξ was found to be independent of the polymer repeating unit, and in the present case of PAAs where the relation between the ξ value and the side-chain length is consistent with a linear decreasing proportionality (figure 7a).

Below T_c (region III), the change in the local polymeric dynamics effective on the length scale of the tracer [15] is observed, which has to be related to the onset of cooperative processes in the polymer chains [33], which are expected to be roughly independent on the side-chain length. However for the ξ' exponents a linear dependence with the mass of the repeating units M_0 of PAAs can be observed (figure 7b) that can be accounted for on the following basis. The ξ' values can be viewed as the product of a cooperative decoupling factor ξ_c with the ξ values coming from steric hindrance. Therefore, the ratio $\xi_c = \xi'/\xi$ should represent the true cooperativity degree on the length scale of the molecular probe [15, 16], and it is actually found to be a constant for the PAAs (figure 7c) according this interpretation.

[Include figure 7 about here]

Conclusions

The dynamics of a nanometric molecular tracer in nearly monodisperse PAA samples of almost the same molecular weight has been studied by ESR spectroscopy. Different dynamical regimes with sharp crossovers have been recognised. In particular, two regions described by the scaling law of equation 5 with different decreasing exponents have been found. Moreover, we have verified that a side-chain independent mechanism is responsible of the crossover from a region to the other, and interpreted this as the onset of cooperativity. Furthermore, the coupling of the probe dynamics to local modes of the host was observed below a temperature T_G , close to the calorimetric glass transition. These results

Probing the cooperative dynamics varying the side-chain length of PAAs

confirm a general scenario already singled out for the cholestane probe dissolved in other polymeric melts.

Acknowledgements

This work was partially supported by Italian MIUR and INFM Pais project.

References

- [1] K. Ngai, *J. Non-Cryst. Sol.* **275** 7-51 (2000).
- [2] P.G. Debenedetti, F.H. Stillinger, *Nature* **410** 259-267 (2001)
- [3] H. Vogel, *Z. Phys.* **22** 641-646 (1921). G.S. Fulcher, *J. Am. Chem. Soc.* **8** 339-345 (1925). G. Tamman, W. Hesse, *Z. Anorg. Chem.* **156** 245-257 (1926).
- [4] C. Hansen, F. Stickel, T. Berger, R. Richert, E.W. Fisher, *J. Chem. Phys.* **107** 1086-1093 (1997); R. Richert, C.A. Angell, *J. Chem. Phys.* **108** 9016-9026 (1998).
- [5] E. Donth, *The Glass Transition* (Springer-Verlag, Berlin, 2001).
- [6] M. Beiner, H. Huth, K. Schroeter, *J. Non-Cryst. Sol.* **279** 126-135 (2001).
- [7] A. Kisliuk, R.T. Mathers, A.P. Sokolov, *J. Polym. Sci. Part B: Polym. Phys.* **38** 2785-2790 (2000).
- [8] L. Berthier, D. Chandler, J.P. Garrahan, *Europhys. Lett.* **69** 320-326 (2005).
- [9] H. Sillescu, *J. Non-Cryst. Sol.* **243** 81-108 (1999).
- [10] O. van der Berg, M. Wübbenhorst, S.J. Picken, W.F. Jager, *J. Non-Cryst. Sol.* **351** 2694-2702 (2005); R. Richert, *J. Non-Cryst. Sol.* **351** 2716-2722 (2005).
- [11] J.Y. Ye, T. Hattori, H. Nakatsuka, *Phys. Rev. B* **56** 5286-5296 (1997).
- [12] J. Bartos, O. Sausa, P. Bandzuch, J. Zrubcova, J. Kristiak, *J. Non-Cryst. Sol.* **307-310** 417-425 (2002).
- [13] M. Faetti, M. Giordano, D. Leporini, L. Pardi, *Macromolecules* **32** 1876-1882 (1999).

Probing the cooperative dynamics varying the side-chain length of PAAs

[14] L. Andreozzi, M. Faetti, M. Giordano, D. Palazzuoli, W. Vittiglio, V. Castelvetro, C. De Vita, *Macromol. Chem. Phys.* **203** 1445-1453 (2002).

[15] L. Andreozzi, M. Faetti, M. Giordano, D. Palazzuoli, G. Galli, *Macromolecules* **34** 7325-7330 (2001).

[16] L. Andreozzi, M. Faetti, M. Giordano, F. Zulli, V. Castelvetro, *Philos. Mag.* **84** 1555-1565 (2004).

[17] L. Andreozzi, M. Faetti, M. Giordano, *J. Phys.: Condens. Matter* **18** 931-940 (2006).

[18] L.H. Sperling, *Introduction to Physical Polymer Science*, third edition (Wiley, New York, 1996).

[19] J.H. Freed, in *Electron Spin Relaxation in Liquids*, edited by L.T. Muus, and P.W. Atkins P. W. (Plenum Press, New York, 1972), p. 387.

[20] L. Andreozzi, M. Giordano, D. Leporini, *Appl. Magn. Res.* **4** 279-295 (1993).

[21] L.T. Muus, P.W. Atkins (editors), *Electron Spin Relaxation in Liquids* (Plenum Press, New York, 1972).

[22] L.J. Berliner (editor), *Spin Labelling: Theory and Applications*, vol 1 (Academic Press, New York, 1976). L.J. Berliner (editor), *Spin Labelling: Theory and Applications*, vol 2 (Academic Press, New York, 1979).

[23] C.P. Slichter, *Principles of Magnetic Resonance* (Harper & Row, New York, 1965).

[24] M. Giordano, P. Grigolini, D. Leporini, P. Marin, *Adv. Chem. Phys.* **62** 321-388 (1985).

[25] M.L. Williams, R.F. Landel, J.D. Ferry, *J. Am. Chem. Soc.* **77** 3701-3707 (1955).

[26] R.G. Larson, T. Sridhar, L.G. Leal, G.H. McKinley, A.E. Likhtman, T.C.B. McLeish, *J. Rheol.* **47** 809-818 (2003).

[27] L. Andreozzi, C. Autiero, M. Faetti, M. Giordano, F. Zulli, *J. Phys.: Condens. Matter* **18** 6481-6492 (2006).

[28] N.G. McCrum, B.E. Read, G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids* (Dover Publications Inc., New York, 1991).

Probing the cooperative dynamics varying the side-chain length of PAAs

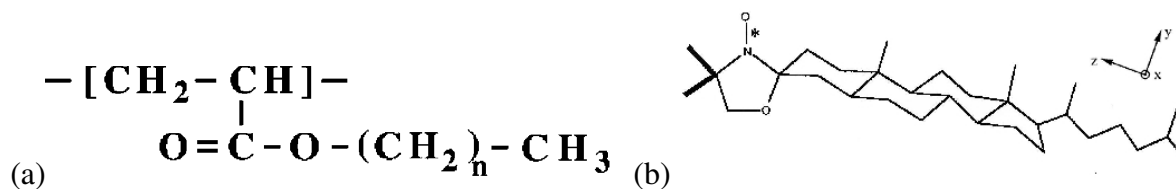
1
2
3 [29] T. Hayakawa, K. Adachi, Polym. J. **32** 845-848 (2000).

4
5 [30] W. Goetze, J. Phys.: Condens. Matter **11** A1-A46 (1999), and references therein.

6
7 [31] J. Bartos, L. Andreozzi, M. Faetti, O. Sausa, D. Rachko, J. Kristiak, J. Non-Cryst. Sol. **in press**
8
9 (2006).

10
11 [32] A. Guillermo, J.P. Cohen Addad, J. Chem. Phys. **116** 3141-3151 (2002).

12
13 [33] M. Guenza, Phys. Rev. Lett. **88** 025901 (2002).
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60



10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

Figure 1. (a) Repeating unit of PAAs and (b) molecular structure of the cholestane spin-probe with its principal molecular frame.

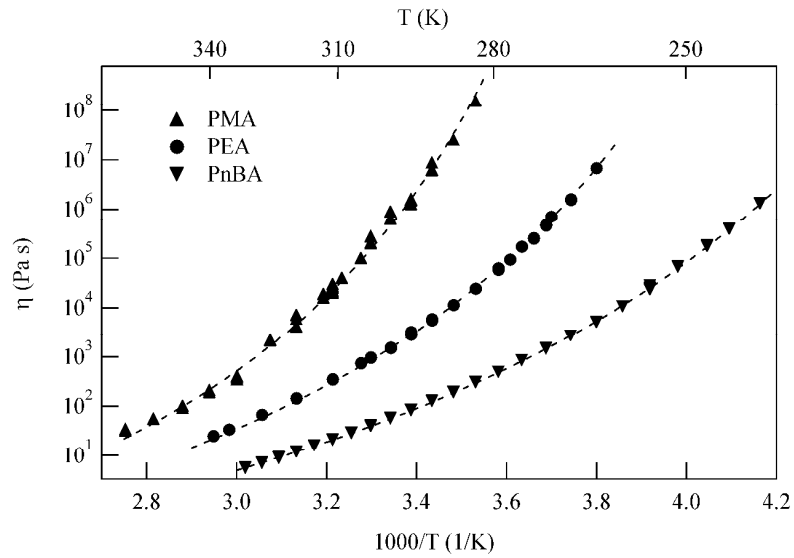


Figure 2. Temperature dependence of the zero-shear viscosity of PAA samples.

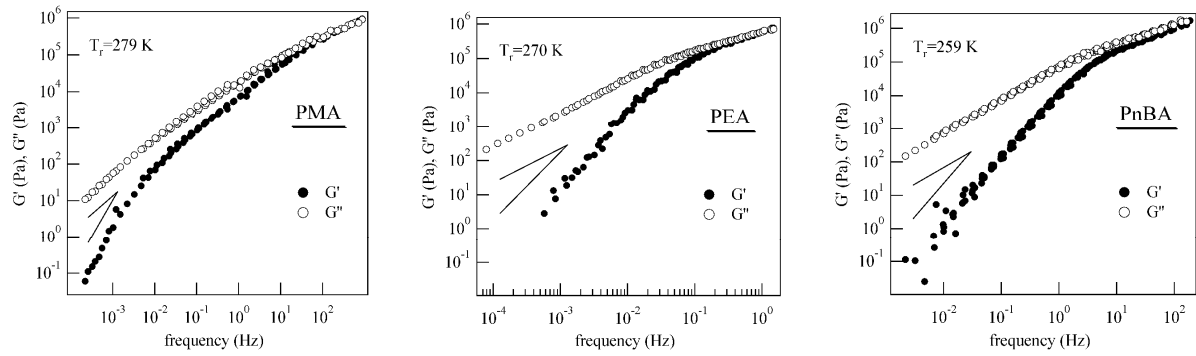


Figure 3. Master curves for the dynamic moduli of PAA samples at the reference temperature

$T_r = 279$ K, 270 K, and 259 K respectively for PMA, PEA, and PnBA.

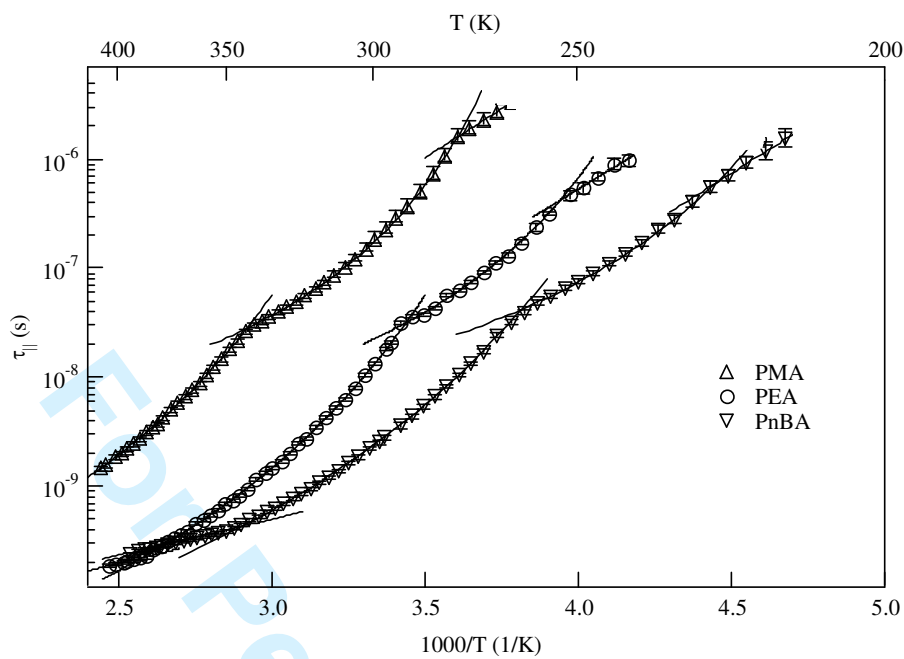


Figure 4. Temperature dependence of the spinning correlation time for cholestane in PAAs.

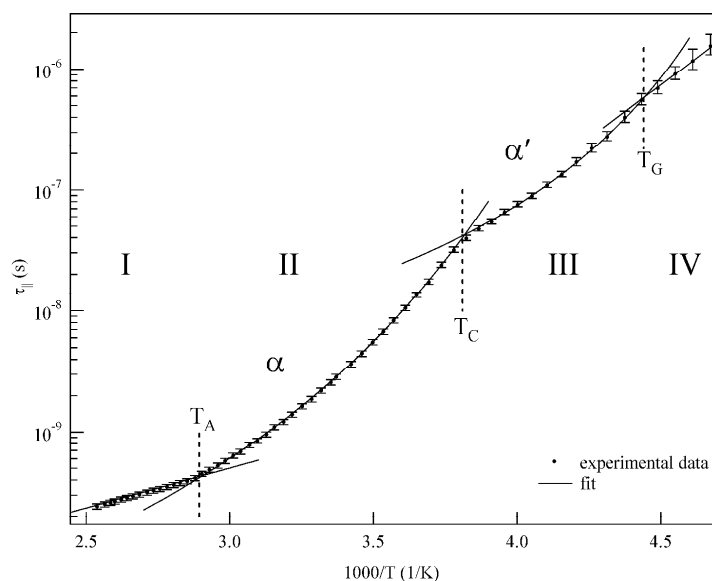


Figure 5. Temperature dependence of the spinning correlation time of the cholestane spin-probe dissolved in PnBA. The superimposed curves are the VF (regions II and III) and Arrh (regions I and IV) laws.

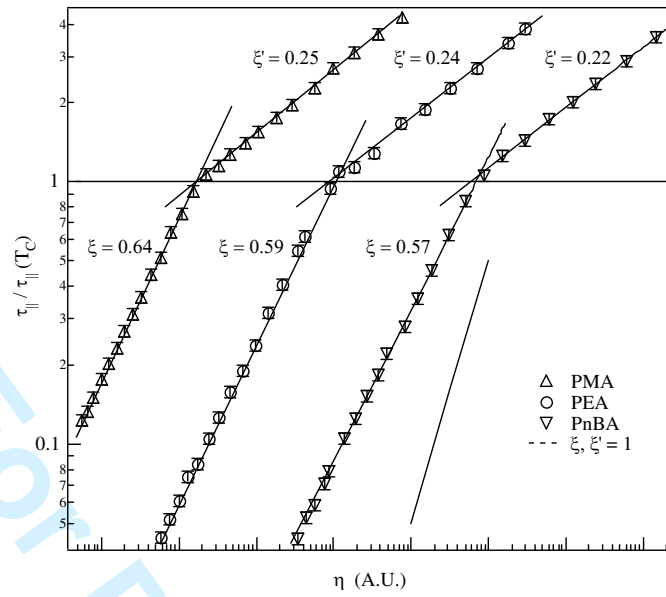


Figure 6. Power law dependence of the spinning correlation time as a function of viscosity for PAA samples. The curves are shifted horizontally to avoid overlap of the data.

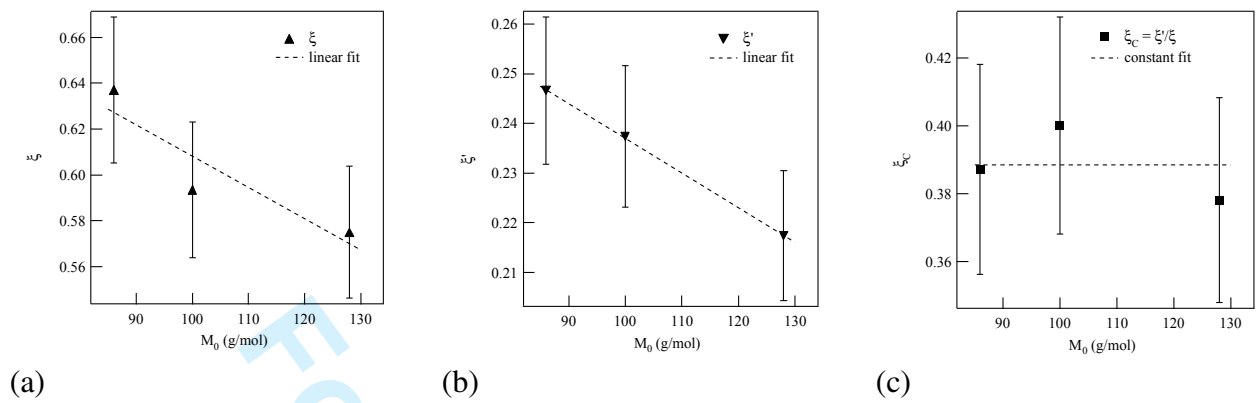


Figure 7. Dependence of the power law exponents (equation 5) and their ratio on the molar mass M_0 of the repeating unit of PAAs.

Table 1. Molar mass data and glass transition temperatures (T_g) of the PAAs. M_w/M_n is the polydispersity index [18], M_0 the molar mass of the repeating unit, M_e the entanglement mass, above which topological features in the dynamics set in [26].

Sample	n	M_n (g/mol)	M_w (g/mol)	M_w/M_n	M_w/M_0	M_e (g/mol)	T_g (K)
PMA	0	13000	14000	1.08	163	11000	272
PEA	1	11600	13100	1.12	131	12000	252
PnBA	3	13000	14700	1.13	115	>13000	224

Table 2. Values of the components of the Zeeman and hyperfine tensors in the principal molecular reference frame for the cholestane probe in PAAs.

g_{xx}	g_{yy}	g_{zz}	a_{xx} (G)	a_{yy} (G)	a_{zz} (G)
2.0033	2.0092	2.0071	33.3	6.2	4.0

For Peer Review Only

Table 3. VF and WLF parameters of PAA samples.

Sample	$\eta_{\infty} \times 10^{-4}$	T_b	T_0	c_1	c_2	T_r	$c_1 c_2 \ln 10$	$T_r - c_2$	c_1^g	c_2^g
	(Pa s)	(K)	(K)		(K)	(K)	(K)	(K)		(K)
PMA	4.3±0.2	1460±30	229±4	12.3	50	279	1410±50	229±2	14	43±4
PEA	8.6±0.8	1430±30	200±4	8.9	69	270	1410±50	201±2	12	52±4
PnBA	6.6±0.2	1425±30	174±3	7.2	86	259	1420±50	173±2	12	50±4

Table 4. Fit parameters for the temperature dependence of the spinning correlation time of
cholestane in PAAs.

Sample	Zone	Temperature Range (K)	Fit Parameters	ΔE	T_b	T_0
				(kJ/mol)	(K)	(K)
PMA	II	$340 \pm 2 = T_C < T$	VF	-	930 ± 40	227 ± 7
PMA	III	$277 \pm 2 = T_G < T < T_C = 340 \pm 2$	VF	-	360 ± 20	227 ± 7
PMA	IV	$T < T_G = 277 \pm 2$	Arrh	34 ± 3	-	-
PEA	I	$T > T_A = 396 \pm 3$	Arrh	13 ± 3	-	-
PEA	II	$290 \pm 2 = T_C < T < T_A = 396 \pm 3$	VF	-	850 ± 40	201 ± 6
PEA	III	$253 \pm 2 = T_G < T < T_C = 290 \pm 2$	VF	-	340 ± 20	201 ± 6
PEA	IV	$T < T_G = 253 \pm 2$	Arrh	35 ± 3	-	-
PnBA	I	$T > T_A = 345 \pm 2$	Arrh	12.6 ± 1.6	-	-
PnBA	II	$262 \pm 2 = T_C < T < T_A = 345 \pm 2$	VF	-	820 ± 40	175 ± 5
PnBA	III	$225 \pm 2 = T_G < T < T_C = 262 \pm 2$	VF	-	310 ± 20	175 ± 5
PnBA	IV	$T < T_G = 225 \pm 2$	Arrh	33 ± 3	-	-

Table 5. Temperatures T_g and T_C , ratios T_C/T_g , and ξ , ξ' , and $\xi_C = \xi'/\xi$ parameters.

Sample	T_C/T_g	T_C (K)	T_g (K)	ξ	ξ'	$\xi_C = \xi'/\xi$
PMA	1.25±0.02	340	272	0.64±0.03	0.25±0.02	0.39±0.03
PEA	1.15±0.02	290	252	0.59±0.03	0.24±0.02	0.40±0.03
PnBA	1.17±0.02	262	224	0.58±0.03	0.22±0.02	0.38±0.03

For Peer Review Only