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Applications of time-resolved luminescence anisotropy measurements to the study of polymer dynamics

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Abstract

Time-resolved (luminescence) anisotropy measurements (TRAMS) may be used to study the dynamic behaviour of macromolecules in a diverse range of systems. The TRAMS approach and its application to studies of the relaxation behaviour of polymers in dilute fluid solution (including aqueous media) and in the solid state are discussed and illustrated by examples from recent investigations in our laboratories.

Keywords: Anisotropy; Fluorescence; Luminescence; Macromolecule; Phosphorescence; Polymer; Relaxation

1. Introduction

The pioneering work of Oster and Nishijima [1] has prompted many investigations of polymer behaviour using luminescence techniques. Luminescence spectroscopy has matured as a versatile and powerful means whereby the properties of macromolecular systems may be probed (see, for example, Refs. [2–4] and references cited therein). In studies of macromolecular dynamics, emission anisotropy measurements are the most informative of the luminescence approaches which can be adopted. Chromophores simply dispersed in the medium of interest can furnish information on the local free volume accessible to the probe, whereas covalently bound labels can reveal intimate details of the kinetic behaviour of chain segments, termini and substituent groups (see, for example, Refs. [4–8] and references cited therein). In this context, time-resolved anisotropy measurements (TRAMS) offer distinct advantages over their steady state counterparts in terms of the amount of detail which can be obtained on the relaxation mechanisms operating in a given system.

In a TRAMS experiment, chromophores (labels or probes) are photoselected during the absorption process from the random assembly present in the system of interest through the use of (vertically) polarized, pulsed radiation for excitation. The resultant time-resolved luminescence is analysed in planes disposed in directions parallel and perpendicular to the incident radiation. The experimental procedure has been described elsewhere (see, for example, Ref. [6]). The resultant emission intensities, corrected [9] for distortions which may be introduced by the sampling system, may be designated as $I_{\parallel}(t)$ and $I_{\perp}(t)$ respectively.

Unravelling the rotational relaxation data encoded in $I_{\parallel}(t)$ and $I_{\perp}(t)$ can be far from trivial; both $I_{\parallel}(t)$ and $I_{\perp}(t)$ will, in general, bear the hallmarks of the excitation pulse leading to their creation. Whilst reconvolution techniques can be applied to derive both the excited state lifetime and rotational relaxation information contained by $I_{\parallel}(t)$ and $I_{\perp}(t)$, problems exist in the recovery of such information (see, for example, Refs. [10–12]).

In principle, the function to be deconvoluted to yield information on the rotational relaxation kinetics (in the absence of the influences of time-dependent energy transfer from the excited states) of the photoselected chromophores is the observed anisotropy $R(t)$ given by

$$R(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} = \frac{D(t)}{S(t)} \quad (1)$$

Unfortunately, direct analysis of $R(t)$ can be unreliable (dependent on the extent to which the finite duration of the excitation pulse and the time responses of the analysis channels involved in recording $I_{\parallel}(t)$ and $I_{\perp}(t)$ distort the latter). Furthermore, reconvolution procedures which might apply to the resolution of time-dependent information contained in $I_{\parallel}(t)$ and $I_{\perp}(t)$ simply do not commute through the division process required by Eq. (1). Fortunately, reconvolution procedures have been developed which allow the functional form of the true emission anisotropy $r(t)$ to be assessed. In impulse reconvolution [13], a mathematical model, descriptive of $r(t)$, is assumed in the generation of a fitting function which

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can be compared with the observed difference curve $D(t)$. In autoreconvolution [14], $I_{\parallel}(t)$ is used in the manner of an "excitation prompt" in the iterative reconvolution analysis of $I_{\perp}(t)$ in a particular application of the general "reconvolution kinetics" [15] approach to data recovery from time-resolved emission information.

We have discussed the various means whereby relaxation information may be recovered from TRAMS data elsewhere (see, for example, Refs. [10] and [11]) and shall not comment further here. It is sufficient to note that, in many situations, such procedures achieve adequate representation of the time-resolved emissions from a labelled macromolecule using a simple, single-exponential model for $r(t)$ of the form

$$r(t) = r_0 \exp(-t/\tau_c) \quad (2)$$

in which r_0 is the intrinsic anisotropy of the chromophore and τ_c is the correlation time characteristic of its motion. Given a suitable means of binding of the label to the polymer, τ_c will be representative of the rotational relaxation of the kinetic unit of the macromolecule that the label is designed to monitor.

In this paper, we illustrate some of the ways in which TRAMS may be applied to the study of macromolecular dynamics by examples drawn from recent investigations undertaken in our laboratories.

2. Experimental details

2.1. Materials

Procedures for the preparation and purification of labelled polymers have been described elsewhere (see, for example, Refs. [11,12,16,17]). In general, the polymers were produced from monomers which had been previously purified by fractional, high vacuum distillation. Free radical polymerizations were performed in solution, typically at 60 °C, under high vacuum. The resultant polymers were purified by multiple precipitation/isolation/dissolution cycles.

Acenaphthylene (Aldrich) was recrystallized from ethanol and triply vacuum sublimated before use. It was incorporated into macromolecules as a label through copolymerization (1 mol.% acenaphthenyl (ACE) or less in feed).

2.2. Instrumentation

TRAMS experiments were conducted at the Synchrotron Radiation Source, CLRC Daresbury Laboratory, UK using the technique of time-correlated single-photon counting.

Table 1
Correlation times τ_c for the intramolecular segmental relaxation of various acenaphthylene-labelled acrylic polymers in dilute solution at 298 K

Polymer[a]	τ_c (ns)	Solvent
PMA	0.7	CH_2Cl_2
PMMA	1.3	CH_2Cl_2
PBMA	2.3	CH_2Cl_2
PAA	1.3	CH_3OH
PMAA	3.7	CH_3OH
PDMAC	1.4	CH_3OH

[a]For definition, see text.

3. Results and discussion

3.1. Segmental relaxation of macromolecules in dilute solution in organic media

The brief existence of the singlet excited states of most organic species (typically tens of nanoseconds) determines the use of fluorescence anisotropy measurements as a means of probing relatively high frequency events. Consequently, fluorescent labels are useful in the study of macromolecular dynamics in fluid media.

Table 1 lists the correlation times associated with the intramolecular segmental relaxation behaviour of various acrylic polymers in dilute fluid solutions at 298 K. The fluorescent label, in each case, is the ACE residue formed by copolymerization of small amounts (less than 1 mol.%) of acenaphthylene. Clearly, the structure of the polymer affects the mobility of the polymer backbone; replacement of the α-proton in poly(methyl acrylate) (PMA) or poly(acrylic acid) (PAA) by a methyl group, yielding poly(methyl methacrylate) (PMMA) and poly(methacrylic acid) (PMAA) respectively, reduces the rate of segmental motion of the macromolecule. However, in neither case is the effect as dramatic as may have been anticipated on the basis of early dielectric relaxation data [18]. It has been reported [18] that the rate of segmental relaxation of PMA in toluene at 298 K is an order of magnitude greater than that of PMMA in the same solvent. However, some caution must be exercised in consideration of the TRAMS data for PMA and PMMA at least, since there is some evidence that the dichloromethane solvent may exert a significant influence on the relaxation behaviour of these systems [12], as discussed briefly below.

The bulk of the ester group also seems to affect τ_c; the rate of backbone relaxation of poly(*n*-butyl methacrylate) (PBMA) is markedly reduced, in dichloromethane, relative to that of PMMA. Again, this observation is unexpected since dielectric relaxation experiments have been reported [18] to show a limited dependence on the nature of the ester substituent for poly(*n*-alkyl methacrylate)s in dilute solution. In contrast, replacement of the acid protons in PAA by $-N(CH_3)_2$ in poly(dimethyl acrylamide) (PDMAC) has little effect on the relaxation rate in dilute methanolic solutions. In aqueous media, on the other hand, PDMAC exhibits a faster

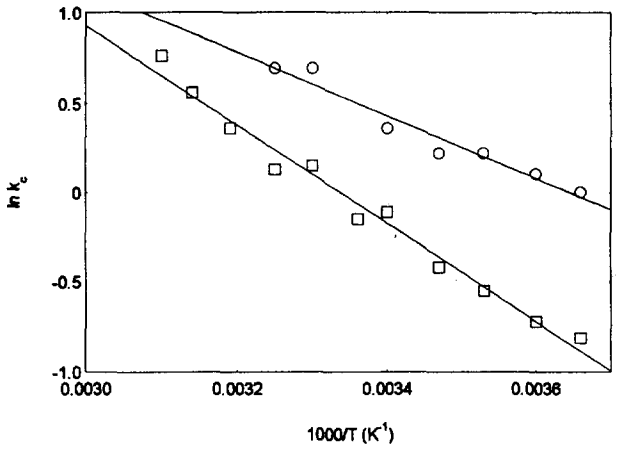


Fig. 1. Temperature dependence of the segmental relaxation behaviour of ACE-labelled PMA in toluene (□) and dichloromethane (○).

segmental motion than that of PAA [8]. Presumably, the hydrogen bonding interactions between the polyacid and water are greater than those of the PDMAC–H_2O system. In addition, the segmental mobility of polyelectrolytes, such as PAA, in aqueous media is dependent, inter alia, on the macromolecule's charge density, as discussed below.

Studies of the temperature dependence of macromolecular dynamics can, in principle, lead to the derivation of "activation energies" characteristic of the barriers to intramolecular segmental motion of a given polymer. In this context, it is normally assumed, following the theoretical approaches of Helfand and coworkers (see, for example, Refs. [19] and [20]) and Kramers' [21] treatment of the passage of a particle over a potential energy barrier in the presence of frictional resistance by a solvent, that the activation energy E_s associated with segmental motion of the polymer is given by

$$E_s = E^* - E_\eta \quad (3)$$

where E^* is the apparent "total" activation energy parameter for the polymer relaxation and E_η is that associated with solvent flow.

Fig. 1 shows the temperature dependence of the intramolecular segmental mobilities (as determined by TRAMS) of PMA in dilute solution in toluene and dichloromethane. Good agreement with Arrhenius behaviour is apparent over the ranges of temperature accessed in each solvent. The resultant energies of activation E^* are approximately 23 and 14.5 kJ mol^{-1} respectively. The errors associated with these estimates are of the order of ± 1.5 kJ mol^{-1}. Compensation for the temperature dependence of solvent flow via Eq. (3) leads to estimates of the activation parameter E_s characteristic of the energy barrier to intramolecular segmental relaxation of PMA of approximately 14.3 and 7.7 kJ mol^{-1} for the polymer dynamics in toluene and dichloromethane respectively.

According to Kramers' [21] theory and its subsequent extension to polymer relaxation [19,20], Eq. (3) should be applicable in the absence of specific polymer–solvent interactions. Furthermore, in the absence of such interactions, E_s should be independent of the solvent. This is clearly not the case in the current instance.

Our estimate of E^* (and thence of E_s) for PMA in toluene is in good agreement with that reported [18] following dielectric relaxation studies of the same system. To our knowledge, there have been no published reports on the macromolecular dynamics of PMA in dichloromethane. However, according to recent TRAMS studies, the intramolecular segmental relaxation of PMMA is also subject to an anomalously large degree of solvent control in dichloromethane [12]. It is probable that dipolar interactions between the ester substituents of each polymer and the chlorinated solvent are responsible for the relatively low apparent barrier to intramolecular rotation E_s observed in dichloromethane. (Alternatively, the relaxation data could be distorted by label–solvent interactions if these were to prove significant. TRAMS studies using fluorescent labels of different chemical types are currently in progress to clarify this point).

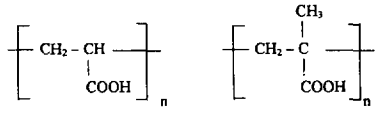
Recently, Ediger and coworkers [22–24] have reported that the local dynamics of both polyisoprene and polystyrene in solution do not exhibit the linear dependence on viscosity suggested by Eq. (3). Adopting an approach similar to that of Fleming and coworkers [25–27], it was proposed that

$$E_s = E^* - \alpha E_\eta \quad (4)$$

where the exponent α governing the viscosity dependence of τ_c is such that $0 < \alpha < 1$. This condition is not satisfied for PMA relaxation within the solvent pair toluene and dichloromethane. However, Eq. (4) would not be expected to hold in the presence of specific polymer–solvent interactions.

3.2. Conformational behaviour of polyacids in dilute aqueous solution

The conformation adopted by a water-soluble polymer in aqueous medium is determined by a complex array of interactions. Hydrophilic constituents of the macromolecule induce polymer–solvent interactions which seek to expand the coil dimensions in solution. Hydrophobic species within the polymer structure produce attractive forces which oppose coil expansion. In the case of polyacids such as PMAA and PAA



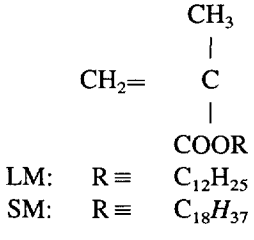
PAA PMAA

the macromolecular conformation is pH dependent. At high pH, the polyacids are fully neutralized and strong coulombic forces of repulsion serve to create extended chain structures which appear, from luminescence measurements [5,8,17], to be relatively open, flexible coils. However, anionic interactions in the polysalts will restrict backbone motion, and the segmental mobilities of the polycarboxylate forms of both PAA and PMAA are less than those of the corresponding polyacids in methanol (as described in Section 3.1).

The macromolecular dynamics of the acid forms of PAA and PMAA show significant differences in aqueous media, which reflect the powerful influence that hydrophobic interactions can exert over the conformational behaviour of polyelectrolytes. In PMAA, the presence of the backbone methyl group induces hydrophobic attractions which, at low pH, cause the acid form of the polymer to "hypercoil" into an extremely compact conformation. Intramolecular aggregation of the methyl groups severely impedes the motion of the chain segments, resulting in rotational correlation times in excess of 50 ns, compared with those of less than 10 ns for fully neutralized PMAA [5,8,16]. PAA, on the other hand, shows a pH-dependent conformational transition which is altogether much less dramatic [5,8].

In earlier reports [5,8,17], we have shown how the hydrophobic modification of PAA and PMAA can alter the intrinsic conformational behaviour of the polyacids and how TRAMS may be used to monitor such changes. In particular, we have reported that hydrophobic monomers, such as styrene and methyl methacrylate, create hydrophobic domains in dilute aqueous solutions of their copolymers with, for example, AA or MAA. These intramolecular aggregates perturb the delicate balance between the contractive and expansive forces which exist in the parent polyacid, shifting the range over which the conformational transition is evident in TRAMS to higher pH. The effects depend both on the nature of the modifying comonomer and its degree of incorporation into the polymer structure [5,8,17].

In the current work, we wish to extend our discussion of TRAMS studies of the effects of hydrophobic modification through copolymerization by reference to recent work on copolymers of lauryl (LM) and stearyl (SM) methacrylates with AA.



In these copolymers, hydrophobic interactions between the long *n*-alkyl chains of the copolymerized esters should result, in dilute polymer solutions, in the formation of intramolecular micelle-like aggregates. Spectroscopic and other solubilization studies (some of which are described below) confirm that such domains are indeed formed [28]. Using suitably labelled copolymers, TRAMS may be used to investigate the effects of these intramolecular hydrophobic agglomerates on the dynamics of the macromolecular "host" which maintains their existence in the aqueous dispersion.

In general, studies involving TRAMS reveal that the incorporation of either LM or SM into AA-based, water-soluble polymers, and the consequent formation of hydrophobic domains, alters the segmental relaxation characteristics of the resultant macromolecule to an extent which depends on the following:

1. the composition of the copolymer;
2. the type of hydrophobic modifier employed (i.e. SM vs. LM);
3. pH.

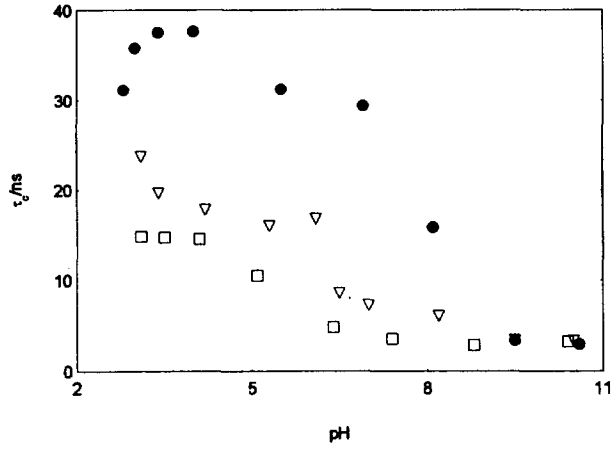


Fig. 2. Dependence of τ_c on pH for ACE-labelled acrylic acid copolymers with styrene (44 mol.% content) (●) and stearyl methacrylate (▽ and □, prepared from polymerization feeds containing 5.7 and 2.6 mol.% stearyl methacrylate respectively).

However, it should be noted that, although the *n*-alkyl chain-based systems exhibit a greater propensity for hydrophobic aggregation than shorter substituents, such as styrene [28], the domains created in the LM and SM copolymers constitute lesser impediments to the motion of the backbone, to which they are appended, than do those of the styrene-modified species. Typical data are shown in Fig. 2.

On inspection of the relaxation data in Fig. 2, it may be tempting to conclude that if hydrophobic domains are created at all, in the SM-modified polyacids, they are not maintained to high pH values. Since solubilization experiments [28] demonstrate that this is not the case, the differences in the effects of hydrophobic aggregation in the styrene-modified systems relative to the SM- and LM-modified systems, on the macromolecular dynamics, must lie in the differences between the domains formed in the different systems. The TRAMS approach, involving solubilized luminescent probes such as pyrene or perylene, can yield information on the viscosity, at the molecular level, of the interiors of the hydrophobic domains created within the coils of modified, water-soluble polymers.

Table 2 lists the correlation times associated with the rotational mobility of a perylene probe solubilized within the hydrophobic cavities formed in dilute (10^{-2} wt.%) solutions of AA polymers incorporating styrene or lauryl methacrylate or stearyl methacrylate as modifying agents. These τ_c values have been recovered in impulse reconvolution [13] analyses in which single-exponential decay functions, of the form described in Eq. (2), were adopted to model $r(t)$, the true anisotropy decay. The anisotropy of the perylene fluores-

Table 2
Correlation times τ_c characteristic of rotation of perylene probes (10^{-5} M) sequestered in the hydrophobic domains formed by various modified acrylic acid polymers in dilute (10^{-2} wt.%) aqueous solution at 298 K

Modifying comonomer (mol.%)	pH	τ_c (ns)
Styrene (44)	4.5	350
	5.5	200
	6.7	33
Styrene (27)	4.0	173
	5.5	73
	6.3	25
LM (7.4[a])	4.1	21
SM (5.7[a])	4.1	55

[a]Copolymer feed composition.

cence is not particularly well characterized by a first-order decay law. This is hardly surprising considering the fact that the fluorescence anisotropy of perylene in fluid media is dual exponential (see, for example, Ref. [29] and references cited therein) and the domain interiors will present any probe with a heterogeneous range of microenvironments. Nevertheless, the τ_c values represent the average correlation times which are more than adequate to provide comparisons between the fluidities of the interiors of the solubilizing domains.

The data presented in Table 2 show that the domains created by the aggregation of the styryl modifying groups restrict the rotational mobility of a sequestered perylene guest to a degree dependent on the pH (and thence on the compaction of the domains themselves). Clearly, the hydrophobic aggregates formed in acid media in the styrene copolymers are much less fluid, as sensed by the perylene probe, than those formed in either LM-modified or SM-modified PAA. It is easy to envisage that the intramacromolecular domains of polyacids modified with long, *n*-alkyl methacrylates may be much less rigid than the aggregates formed between styryl residues, and thence exert a lesser effect on the chain dynamics of the polyacid in the "polysoaps". The current probe data are consistent with such a representation of the domains formed in these different types of modified PAA.

3.3. Relaxation in the polymeric solid state

Emission anisotropy experiments can provide information on relaxation phenomena in the bulk phase. Fluorescence anisotropy measurements may be used to probe high frequency processes in, for example, polymer melts [7,29,30]. If, however, the purpose of the experiment is to gain information on the molecular processes leading to the various relaxations apparent in a given bulk polymer, it is better to work at lower frequency ranges wherein the individual transitions may be (better) resolved. Phosphorescence anisotropy measurements present an opportunity to study the polymeric solid state in such a manner. However, there are problems in applying the phosphorescence version of the luminescence anisotropy technique.

The triplet states which give rise to phosphorescence in aromatic chromophores are very sensitive to the rigidity of the surrounding matrix. Consequently, phosphorescence intensity and lifetime measurements have been used [31–36] to detect transitions in polymers. However, anisotropy measurements are necessary to yield information on the dynamic behaviour of the macromolecules during these transitions. Unfortunately, the sensitivity of the triplet excited state to its microenvironment markedly reduces the emission intensity to be sampled in the vicinity of a major relaxation process, such as the glass transition. Nevertheless, there are a few reports of the use of steady state phosphorescence anisotropy to study bulk synthetic polymers [33–35] but, to our knowledge, none to date involving TRAMS in phosphorescence.

Given the potential of the technique to yield useful information on the relaxation mechanisms and dynamics of a particular polymer in a matrix, it is worthwhile to persevere with time-resolved phosphorescence anisotropy. Fig. 3(a) and (b) show the intensities of phosphorescence from a vinylnaphthalene-labelled sample of PMA analysed in planes parallel ($I_\parallel$) and perpendicular ($I_\perp$) to that of the vertically polarized excitation using a time-resolved phosphorescence spectrometer described elsewhere [36].

At 283 K, the conventional glass transition temperature of the polymer [37], very little relaxation of the phosphores-

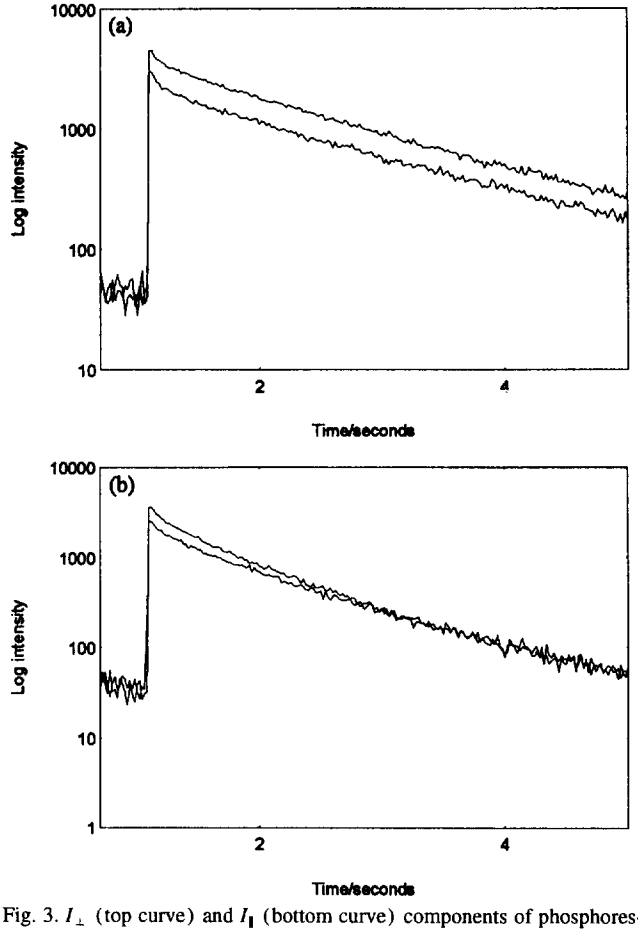


Fig. 3. $I_\perp$ (top curve) and $I_\parallel$ (bottom curve) components of phosphorescence emitted from 1-vinyl-naphthalene-labelled PMA at 283 K (a) and 298 K (b).

cence anisotropy is apparent within the luminescence lifetime (Fig. 3(a)). At higher temperatures, the phosphorescence anisotropy clearly decays with time, as shown for 298 K in Fig. 3(b). The time-resolved phosphorescence anisotropy approach is obviously capable of yielding information on polymer dynamics in the solid state, and experiments in this area are continuing in our laboratories.

4. Conclusions

The TRAMS technique can yield valuable information on polymer relaxation both in solution and the bulk phase. Fluorescence anisotropy, constituting a high frequency test procedure, is well suited to the study of the intramolecular segmental mobility of polymers in dilute fluid solutions. Investigation of relaxation mechanisms in the polymeric solid state is perhaps more readily accomplished using phosphorescent, rather than fluorescent, species as interrogators of macromolecular behaviour.

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