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DEVELOPMENT OF POLYMER CHARACTERIZATION FROM TIME-AVERAGED TO TIME-DEPENDENT PROPERTIES

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Abstract - Over the years, as different polymer properties have become important, molecular characterization has developed from time- and ensemble-averaged size determination, adding stereochemical information, to include a variety of time-dependent molecular transport properties.

INTRODUCTION

Twenty five years ago the phrase 'polymer characterization' was taken to mean almost exclusively the determination of molecular weight, and an estimate of its distribution by comparison of number, weight and Z-average values. The more pedantic amongst us might have included the broad chemical classification such as monomer type, and possibly some dimensional characteristic, but generally we were concerned with size, averaged both in time and over a molecular ensemble.

The decade between the mid-50s and mid-60s witnessed three coincidental developments. There was the growth of interest in the chiral properties of organic molecules, and the ability to characterize these by new spectroscopic techniques of which nuclear magnetic resonance was important. In polymer science the use of Ziegler-Natta catalytic systems produced an enormous range of polymers the physical characteristics of which were very dependent on the stereochemistry of the many chiral centres in the backbone chains. Consequently the philosophy of polymer characterization took on some of the spectroscopic ethos of the period, and came to include the determination of stereoregularity. The configurations of chiral centres on a normal organic polymer are essentially invariant on any normal time scale, and so in this era characterization still concentrated upon time and molecular averages of the properties of interest.

During the 1960s a technique which had been known for many years and had become standard in biochemistry suddenly exploded in importance for polymer characterization. This was gel permeation chromatography, and by its use distributions within a molecular average became readily available. Of course the technique has to be standardised, and it discerns primarily molecular volume, but nevertheless it does allow simple and reliable determination of molecular weight distributions. The use of multiple detection techniques permitted the evaluation of multi-dimensional (e.g. chemical composition and molecular weight) distributions, and so the restriction of philosophy to ensemble averages was lifted. This trend has continued to the present day embracing the development of more sophisticated spectroscopic techniques which probe with increasing resolution the particular environments of selected groups on the polymer chains.

Looking back to these days it is immediately apparent that polymer characterization has sought those molecular properties which distinguish macromolecules from their low molecular weight analogues. Obviously these are sheer size, and the possibilities for arrangement of distinguishable units in a molecule made up of many such units. There is no great philosophical step between what a molecule is and what a molecule does. In truth there is not really any philosophical divide between what a molecule does and what a macroscopic sample does. However, it is my personal view that polymer characerization today has take the first of these steps, but not the second, so that the subject remains one of determining molecular characteristics, but now includes certain basic behavioural properties. These, needless to say, are time-dependent. So, in our present understanding, the restriction to time and ensemble averages is lifted.

TIME-DEPENDENT CHARACTERISTICS

Since the chemical structure and stereo-configuration of a macromolecule are essentially time invariant, the most obvious time-dependent property (by analogy with small molecules) is the conformational structure of the chain sub-units and of the chain as a whole. The early observations of macromolecular chain dimensions were, of course, time and ensemble averaged conformational characterization. So too were studies of tertiary structure such as helix-coil analyses. However today we are concerned with observation and characterization of time-dependent conformational behaviour. This has two related objectives, being the conformational property itself as a component in the identity of a macromolecule, and observation of the property as a measure of some other structural characteristic.

(a) Characterization of Conformational Dynamics

Techniques of characterizing time-dependent conformational changes fall into two classes, those which probe the behaviour of localised units of the macromolecule and those which sense changes in the overall dimensions of the macrochain. In the former category come spectroscopic techniques sensitive to specific atoms, bonds or groups, and relaxation techniques in which the overall response can be attributed to localised interactions of the molecule with the appropriate field or constraint. In the latter are phenomena where the phase-coherent motions of the whole chain interact with some sensing field or perturbation, the best known example of which is liquid viscosity. Scattering phenomena bridge this somewhat arbitrary division, since small scattered particles such as neutrons probe localised motions, whereas larger scattered particles such as long wavelength photons are more sensitive to coordinated whole-molecule motions. This division into localised segmental motion (in which there may or may not be a phase coherence between the motions of individual chain units) and the whole molecule translation, rotation and distortion is an important one. Characterization of the localised motions gives us a deeper insight into the basic question as to whether a chain is *flexible* or *stiff*. Prior to the development of time-dependent studies a flexible chain was simply one in which the coiled backbone exhibited a small end-to-end separation, while a stiff chain was characterised by a large end-to-end separation. The introduction of ease of conformational change (both in the energy required and the speed of change) brings to the characterization of macromolecules the full significance of these words.

Relaxation techniques, in which the time-dependent return to equilibrium of some property is observed after a change in the constraints acting on the system, measure a variety of dynamic conformational processes, Table 1, figures 1, 2. Since the effects of chemical structure are minimised in normal mode processes, from the point of view of characterization it is the localized or segmental processes which are of greater interest.

TABLE 1. Some relaxation phenomena associated with molecular movement

Phenomenon	Constraint varied	Property observed	Motion involved
Dynamic mechanical relaxation	Stress, strain	Strain, Stress, Modulus	Translation and rotation of molecules and chain segments
Viscoelastic relaxation	Shear stress, shear rate	Dynamic viscosity, shear modulus	Translation and rotation of molecules and chain segments
Ultrasonic relaxation	Pressure, temperature	Acoustic absorption, velocity	Any molecular change for which either $\Delta V^{\ddagger} \neq 0$ or $\Delta H^{\ddagger} \neq 0$, e.g. conformation change
Dielectric relaxation	Electric field	Electric polarization, capacitance, loss	Limited translation of charges, rotation of dipoles

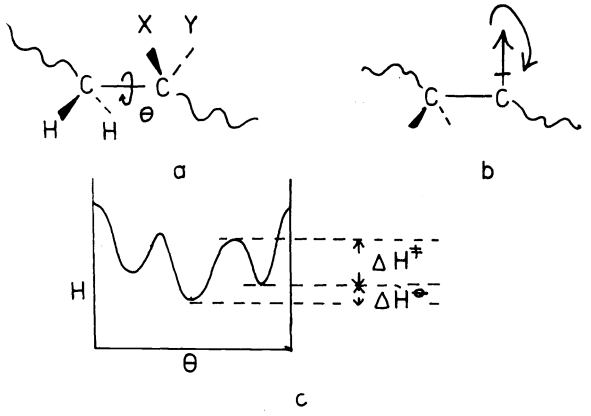

Fig. 1. LOCALIZED MODE
(a) Bond Rotation
(b) Dipole Orientation
(c) Conformational Energetics

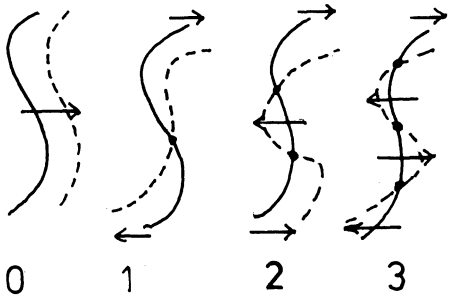

Fig. 2. NORMAL MODES OF MOTION
(Phase-Coherent Conformation Change)

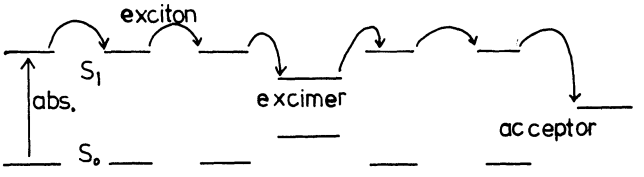

Fig. 3. Energy Level Diagram for Exciton Movement along a Chain of Chromophores

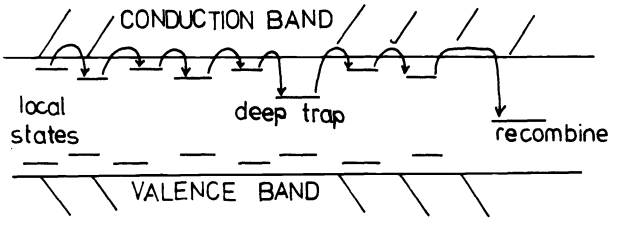

Fig. 4. Energy Level Diagram for Electron Movement across a Sequence of Molecules

TABLE 1/cont.

Phenomenon	Constraint varied	Property observed	Motion involved
Fluorescence depolarization	Polarized electromagnetic field	Polarized fluorescence	Rotation of electronic transition dipole moment
Nuclear magnetic and electron spin relaxation	Magnetic field	Nuclear and electron spin magnetic polarization	Rotation of particle spin transition moment

Some chain flexibilities measured by dielectric relaxation are presented in Table 2.

TABLE 2. Form of certain polymers

Polymer	Flexibility
Poly(methyl methacrylate)	Flexible coil
Poly(vinyl chloride)	Flexible coil
Cellulose esters	Stiff coil
Poly(N-vinyl carbazole)(molecular weight > 10^5)	Flexible coil
Poly(N-vinyl carbazole)(molecular weight < 10^4)	Stiff coil
Poly(n-butyl isocyanate)(molecular weight 10^4)	Stiff rod
Poly(n-butyl isocyanate)(molecular weight 10^5)	Stiff coil
Poly(γ-benzyl L-glutamate (α-helix)	Stiff rod
DNA (molecular weight< 10^5)	Stiff rod
DNA (molecular weight > 10^6)	Stiff coil

Since dielectric relaxation measures the orientation of the resultant electric dipole, summing the contributions of each of the segment dipoles, the observation senses only that process by which the resultant reorientation is most easily reached. For small molecules whole-molecule rotation might be faster than conformational rearrangement, and so the molecule is sensed as a rigid sphere or coil. On the other hand, for infinitely large molecules even a slow conformational rearrangement will be faster than whole molecule rotation, and the motion will be sensed as flexibility of the chain. So this definition of flexibility must be qualified with a note of the chain length involved. By the same token, a slightly curved rod-like molecule, if built up to sufficient size, will take on a coil-like shape even although the radius of curvature is large. The reorientational characteristics of rods and coils are significantly different. Both of these size effects can be seen in Table 2.

Turning now to the energetics of localized conformation change, some enthalpy differences between the two most stable rotational isomeric states measured in solution by acoustic techniques are illustrated in Table 3, and some activation energy barriers to segmental rotation in solution, again measured acoustically, are given in Table 4. The two state enthalpy differences of Table 3 are particularly interesting since formally these correspond to the Gibbs-Di Marzio flex energies determining the glass transition temperature in the solid state. The larger $\Delta H^{\ominus}$ for poly(α-methyl styrene) than polystyrene is in accord with the higher Tg of that polymer, and the $\Delta H^{\ominus}$ for isotactic poly(methyl methacrylate) lower than the syndiotactic form is also as expected from their different Tg's.

TABLE 3. Effect of structure on rotational isomeric parameters

Polymer	Tacticity	ΔH^{Θ} kJ mol^{-1}
Poly(methylmethacrylate)	Isotactic	3.7
	Syndiotactic	6.3
Poly(α-methylstyrene)	Syndiotactic	8.7
Polystyrene	Atactic	5.4

TABLE 4. Activation energy of rotational isomerism

Polymer	Tacticity	$\Delta H^{\ddagger}$ kJ mol^{-1}
Poly(ethylene)		4-6
Poly(ethyleneterephthalate)		4-6
Poly(oxymethylene)		6
Poly(methylmethacrylate)	Isotactic	17
	Syndiotactic	20
Poly(methylacrylate)	Isotactic	7
	Syndiotactic	3
Poly(propylene)	Isotactic	4-5
	Syndiotactic	3.4

In Table 4 we can see how the energy barrier reflects the steric constraints around the most flexible links in the backbone. Thus comparison of the acrylates and methacrylates shows how methyl substitution hinders rotation about bonds connecting to the methylene - CH_2 - group, and the low value for poly(ethylene terephthalate) illustrates the relative freedom of the ester linkage.

These relaxation techniques measure localized properties averaged over all the units in all the molecules, so that they are ensemble averages. The development of spectroscopic techniques has given us the ability to examine the conformational properties of specific units in the chain. Thus spectrofluorimeters are now so sensitive that observations can be made of a single chromophore in a polymer chain. Then observation of fluorescence depolarization of chromophores in different specific locations can be used to measure the different rotational freedom of these positions, such as chain interiors and chain ends, Table 5.

Perhaps more exciting is the way that observation of ^{13}C nuclear magnetic relaxation times can now characterise the dynamic behaviour of carbon atoms in specific positions. Thus the artificiality of introducing a foreign chromophore group is avoided. An example of the type of information now available is given in Table 6 and the subject is treated in greater detail later in this conference.

TABLE 5. Rotational times of fluorescent chromophores on polymers dissolved in toluene at 298K.

Polymer chain	Chromophore and position	Rotational time ns
Poly(butyl methacrylate)	Anthracene - chain end group	0.8
	Anthracene - side group in chain interior	4.0
Polystyrene	Anthracene - chain end	0.8
	Anthracene - side group in chain interior	6.0
	Naphthalene - side group in chain interior	5.5
Poly(N-vinyl carbazole)	Anthracene - side group in chain interior	26

TABLE 6. ^{13}C nuclear magnetic spin lattice relaxation times in two alkanes

$\underset{1}{CH_3} - \underset{2}{CH_2} - \underset{3}{CH_2} - \underset{4}{CH_2} -$

	T_1/s			
Molecule	C_1	C_2	C_3	C_4
n-Hexane	21	15	16	16 ($C_4 = C_3$)
n-Hexadecane	6.5	3	2.4	1.7

(b) Time-dependent characterization of structural parameters

An interesting example of the way in which the increasing sophistication of time-dependent observations has aided the characterization of familiar structural parameters is provided by quasi-elastic light scattering. The light scattered by a polymer molecule in solution is Doppler shifted by the various motions of the molecule. It is possible now to measure the frequency broadening of the scattered light, and to relate it to the translational diffusion coefficient of the macromolecule. This can be done with such precision that quite fine comparisons of hydrodynamic radii and shape factors can be made, as exemplified in Table 7.

TABLE 7. Diffusion coefficients determined by quasi-elastic light scattering, polystyrene $\bar{M}_w$ 1.62 x 10^5 at 298K

Solvent system	D x 10^{11} /m² s^{-1}
Benzene, zero concentration	3.6
Benzene, polystyrene 8.9% w/v	10.0
Benzene, poly(methylmethacrylate) 7% w/v polystyrene 0.1% w/v	1.0

CHARACTERIZATION OF PHOTO-ELECTRIC PARAMETERS

As new uses for polymers are developed, so different properties may become important and consequently new characterization techniques emerge. An interesting example of such a phenomenon can be seen in the development of new electrical uses for polymeric materials.

The very first use of polyethylene was as an electrical insulator, and the rapid development of electronic equipment during World War II meant that polymers became firmly established as dielectric materials. As a result, the use of dielectric methods to establish the permittivity and loss of such materials became standard. This led quite naturally to dielectric relaxation being a means of investigating macromolecular behaviour as well as being a characterization technique. As telecommunication equipment has developed towards ever higher frequencies, so too have the required characterization methods moved from simple resistance-capacitance bridges to sophisticated waveguide techniques. Nevertheless the emphasis has always been on the use of the polymer as an insulator.

Over the last two decades, however, a number of devices have been invented which utilize the conductance properties of polymers. Probably the most familiar of these is the electrostatic photocopying machine in which the creation of an image pattern of electrostatic charge depends (in part) upon photoconduction of charge carriers through polymeric material. Present interest in ways of utilizing solar energy has also given a tremendous boost to research into the photovoltaic and photogalvanic properties of polymers.

Characterization of polymers for such uses is complex, because both photo and electric aspects must be determined. Present philosophy is to try and unify these aspects by looking at the transport and trapping of both the energy incident in the original photon and the charge carrier which may be generated or mobilised by it. The language of solid state physics is thus starting to be heard in characterization circles, with talk of exciton traps (the places in the polymer chain or polymeric material where the mobile packet of excitation energy becomes immobilised) and exciton transport coefficients (the diffusion coefficient of the mobile energy discussed as if it were a molecule or a charge carrier). In this way the primary photophysical processes are characterized in terms of an energy level diagram, figure 3, remarkably similar to that for transport of electrical charge carriers, figure 4. An example of such characterization, poly(N-vinyl carbazole) is given in Table 8.

TABLE 8. Photoelectric characterization of Poly(N-vinyl carbazole)
Mobile species : incoherent exciton and positive hole

Property	Exciton	Hole
Formation energy	360 kJ mol^{-1}	-570 kJ mol^{-1}
Migration coefficient	8 x 10^{-9} m^2 s^{-1}	1 x 10^{-11} $m^2V^{-1}s^{-1}$
Activation energy for escape from trap	17 kJ mol^{-1} (excimer dissociation)	12 kJ mol^{-1} (carrier hopping)

For this material the excitation energy jumps from carbazole unit to carbazole unit in a sequence of hops, and so is said to be transported as an incoherent exciton. It is momentarily localized in rather shallow excimer (excited state dimeric complex) traps. Conductivity is by holes in the valence band which have high energies of formations and low mobility. However, the mobility is increased by many orders of magnitude when the material is doped.