Chapter 4

DYNAMICS OF POLYMERS BY NEUTRON SCATTERING

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SUMMARY

Using the latest high resolution spectrometers, neutron scattering explores molecular motion at frequencies between $10^7$ and $10^{14}$ Hz. This includes vibrations and rotations of side groups, phonon modes in crystals and high frequency conformational changes in solutions, melts and networks. The random variation in scattering power from nuclide to nuclide allows labelling techniques to be used to advantage, while the large neutron mass leads to a relatively short wavelength at low energies (compared to electromagnetic radiation) and gives spatial information simultaneously with the frequency information.

The basic theory of neutron scattering is developed and then applied to calculations for models of polymeric motion. The specific techniques of use in observing polymeric motion are briefly described. A number of experimental examples are discussed where neutron spectroscopy has provided new information on motion of side groups or of the chain backbone.

1. INTRODUCTION

Motion of polymer molecules occurs over many decades of frequency from the slow reorientation of whole molecules in melts just above their glass
transition temperatures \((T_g)\), which may take weeks or even years, to the
torsions and vibration of side groups at around \(10^{14}\) Hz. As will be seen, the
neutron technique\(^{1-4}\) samples only the upper end of this range with a limit
which has currently been pushed down by the ultra-high resolution spin-
echo spectrometer to around \(10^7\) Hz. Within this range fall the molecular
vibrations of side chains, the rotations of such side groups, the travelling
waves in crystalline samples and the higher frequency backbone motions of
polymers in solution and in melts at temperatures well above \(T_g\).

There is considerable overlap in the information obtained with tech­
niques such as NMR relaxation measurements,\(^5,6\) IR and Raman spectro­
scopy,\(^6\) high frequency viscoelastic\(^7\) and ultrasonic measurements.\(^8\)
However, the unique feature of the neutron scattering technique is that the
relatively heavy neutron has large momentum at modest energies. The
wave vector changes associated with energy transfer are important and
neutron experiments explore regions of momentum transfer (\(Q\)) space
away from the \(Q \approx 0\) region of IR and Raman spectroscopy. Neutron
scattering spectra inherently convey direct information about spatial
correlations as well as energy fluctuations in a way not available from the
other techniques mentioned. In addition, the neutron interacts directly
with the scattering nuclei (no optical selection rules) and this interaction
varies from isotope to isotope (in particular, there is a large difference
between hydrogen and deuterium) thus allowing labelling techniques to be
used.

Despite these compelling advantages, neutron scattering has not been
extensively applied to the study of polymer dynamics. This is partly
because the highest resolution spectrometers have only recently been
available and partly because the necessity of taking the sample to the
neutron source has meant spectrometers have appeared relatively inac­
cessible to polymer scientists.

The types of motion mentioned above cover a fairly broad range and, as
can be imagined, demand rather different spectrometers for their
observation. Four typical spectrometers which cover the required range
between them are described in Section 3. A brief summary of the basic
theory of the technique is given in Section 2, together with the models of
polymer motion commonly used to interpret the neutron data. Sections 4
and 5 then attempt to survey the field of applications by discussing
examples of particular problems where neutron scattering techniques have
proved to be useful.