11 Urethane-based dispersions
H. REIFF and D. DIETERICH

11.1 Introduction

11.1.1 Linear segmental polyurethanes

Since their invention in 1937, polyurethanes have been developed to be the most extensive and versatile class of polymers. The main reason for this is the rich choice of starting materials (‘building blocks’) which can be combined by the diisocyanate polyaddition process.

The remarkable physical properties of most polyurethanes are based on a segmental primary structure \((A-B)_n\). The so-called ‘soft’ segment is usually a polyether or polyester macrodil, while the ‘hard’ segment consists of an (oligo)-urethane unit or an (oligo)-urea unit, built up from diisocyanates and ‘chain-lengthening agents’ such as short-chain diols, diamines or water. Thus a segmental polyurethane consists of at least three components (Figure 11.1).

The soft segment and hard segment differ not only in ‘hardness’ and flexibility but also in polarity, compatibility and interchain interaction. In a typical thermoplastic polyurethane elastomer, the soft segment is > 50% by weight, forming a continuous matrix, in which the hard segments aggregate to microdomains with high cohesion. These microdomains are physical cross-linking sites which reversibly ‘disappear’ at the melting temperature of the hard segment domains and are responsible for the thermoplastic character.

11.1.2 Polyurethane ionomers

In the architecture of polymers, ionic sites seem somewhat exotic in an organic hydrophobic neighborhood. Exactly this unusual combination, however, of a few highly polar ionic centers in a relatively unpolar macromolecular environment characterizes an ionomer. The ionic sites may be located within the backbone (e.g. quaternary ammonium groups) or pendant (e.g. sulfonate or carboxylate groups).

When incorporated into the hard segment, the distance to the next ionic site is roughly the length of the soft segment. Introduction of ionic groups into the soft segment leads to an equal and even distribution.
As outlined above, most polyurethanes have a segmental structure before the transformation into an ionomer. There is a substantial difference therefore in whether the ionic site is within the soft segment or within the hard segment. Accordingly the property pattern is different.

Polyurethane ionomers usually contain 10–120 meq of ionic groups per 100 g of polymer. The soft segments between them are predominantly hydrophobic, the molar mass ranging from 600 to 5000. By contrast, polyurethane polyelectrolytes contain 200–400 meq of ionic groups. Hydrophobic segments normally do not exceed a molar mass of about 300–500.

There is presently a worldwide interest in polyurethane ionomers and consequently an increasing effort in research and development.

### 11.1.3 A scientific challenge

An ionomer combines organic macromolecular chemistry with the inorganic chemistry of salts. Both seem incompatible with each other. Their combination in one macromolecule prompts expectations of novel physical effects and to interesting properties of polyurethane ionomers.

Normally, segmental polyurethane ionomers contain polyether or polyester chains of low polarity, urethane groups, often urea groups, both of which are polar and capable of interchain interaction via hydrogen bonding. Ionic groups can be cationic, anionic or zwitterionic and counterions may vary widely. All these groups can—to a different degree—interact with each other. Ionic sites tend to aggregate, but are linked to an ‘alien’ hydrophobic