

# ***Aqueous Solutions of Poly(N-isopropylacrylamide)***

## **INTRODUCTION**

Poly(methacrylic acid) differs from the closely related poly(acrylic acid), polyacrylamide and polymethacrylamide in that it forms gel in aqueous solutions at sufficiently high concentrations. Its solutions separate into two phases upon heating,<sup>1</sup> and it has a negative entropy of dilution and an exothermal heat of dilution.<sup>2</sup> Changes in the dilute solution viscosity of its solution upon addition of cosolutes differ from those of the other three polymers.<sup>3</sup> Negative thixotropy is also peculiar to poly(methacrylic acid).<sup>4</sup> These features have been explained in terms of hydrophobic bonding.<sup>5</sup> More recently,<sup>6</sup> it was found that aqueous solutions of poly(N-isopropylacrylamide), like those of poly(methacrylic acid), separate into two phases upon heating and the intrinsic viscosity decreases with increasing temperature. It is therefore likely that there are other features common to these two polymers. The objective of the present research is to detect these common features.

## **POLYMERIZATION OF N-ISOPROPYLACRYLAMIDE**

N-Isopropylacrylamide was polymerized in benzene with benzoyl peroxide at 50°C. The resulting gel was dissolved in acetone, from which the polymer was precipitated by adding an equal volume of water. [Poly(N-isopropylacrylamide), like polyacrylamide, is insoluble in acetone-water mixtures but differs from the latter by being readily soluble in pure acetone.] Dissolution in acetone and precipitation with water were repeated in order to purify the polymer, after which the polymer was dried in vacuo at room temperature. Its intrinsic viscosity in water at 30.0°C was  $[\eta] = 55 + 0.089c$  (cc/g).

## **PROPERTIES OF CONCENTRATED SOLUTIONS**

Aqueous solutions of poly(N-isopropylacrylamide) up to about 10% did not show elastic properties at room temperature and separated into two phases near 35°C. More concentrated solutions (10%–25%) at room temperature, up to about 26°, displayed spinnability and an extremely strong Weissenberg effect.<sup>7</sup> In this respect, they resembled solutions of poly(methacrylic acid) but, unlike these, they showed no negative thixotropy. [A 22% aqueous solution of polyacrylamide (mol. wt 480,000) did not display any elastic properties.] At 28°–30°, the solutions of poly(N-isopropylacrylamide) became turbid and turned into stiff gels; this thermal gelation is perfectly reversible (phase separation occurs at higher temperatures). Thus, in solutions of poly(methacrylic acid), concentration is the most decisive parameter in causing gelation, a 1% increase causing a change from an elasticity-free liquid to a rigid gel.<sup>1</sup> In the case of poly(N-isopropylacrylamide) above a certain value, concentration does not have a marked effect on elasticity. On the other hand, increase in temperature, which causes only a moderate increase in the elasticity of poly(methacrylic acid) solutions, brings about a sol-gel transition in poly(N-isopropylacrylamide). This difference is in accordance with the behavior in dilute solutions. Whereas it appears from light-scattering measurements that poly(methacrylic acid) exists in dilute solutions in the form of individual hypercoiled molecules, poly(N-isopropylacrylamide) molecules associate strongly near the lower critical solution temperature, even in very dilute solutions.<sup>6</sup>

## **EFFECT OF COSOLUTES**

The addition of 1% sodium dodecyl sulfate causes a strong increase (from 55 to 225 cc/g) in the intrinsic viscosity of poly(N-isopropylacrylamide). Moreover, whereas the polymer is precipitated from a dilute aqueous solution at about 35°, in the presence of 1% sodium dodecyl sulfate it remained in solution even upon boiling. Thus, in its response to sodium dodecyl sulfate, poly(N-isopropylacrylamide) differs strongly from polyacrylamide and polymethacrylamide, which do not interact with sodium dodecyl sulfate.<sup>8</sup> In this respect, it resembles poly(methacrylic acid), poly(acrylic acid), poly(vinyl alcohol), poly(vinylpyrrolidone),<sup>9</sup> and poly(ethylene oxide).<sup>10</sup> The interaction with

sodium dodecyl sulfate is ascribed to hydrophobic bonding.<sup>11</sup> Poly(N-isopropylacrylamide) did not interact with Congo Red; in this respect it differs from poly(vinyl alcohol) and poly(vinylpyrrolidone).

The hydrogen-bond breaking agents LiCl (6*M*) and urea (5*M*), which cause a large increase in the intrinsic viscosity of polymethacrylamide<sup>12</sup> and do not affect that of polyacrylamide, cause the precipitation of poly(N-isopropylacrylamide) from dilute solutions at 30°. In worsening solubility by urea, poly(N-isopropylacrylamide) resembles poly(methacrylic acid), and there seems to be no pronounced hydrogen bonding in aqueous solutions of poly(N-isopropylacrylamide).

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JEHUDAH ELIASSAF\*

The Laboratory for Organic and Biological Chemistry  
The Hebrew University  
Jerusalem, Israel

Received December 22, 1976  
Revised January 21, 1977

\* Present address: 9 Asher St., Haifa 32 297, Israel.