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EPR spin probe study of polymer associative systems

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Abstract

Molecular dynamics of polyacrilamide gels, polymeric micelles and hydrogel of polyacrylic acid and macrodiisocyanate was investigated by the ESR spectroscopy of spin probes. The local mobility in network junction of polyacrylamide gels is found to be essentially slower than that in the micelles created by the low molecular weight detergents and does not depend on the amount and length of hydrophobic groups (C9 or C12) in the polymer chain. The immersion of 10–30 mol.% of ionic monomers into the polymer chain (sodium acrylate) influences insufficiently on the local mobility of network junctions. In aqueous solutions, polystyrene-block-poly-(*N*-ethyl-4-vinylpyridinium bromide) block copolymers create polymeric micelles. The local mobility in the polystyrene core of the micelles is about twice as much as that in the solid polystyrene. Partially swellable polymer network in aqueous solutions was synthesized from polyacrylic acid and macrodiisocyanate. The local mobility in hydrophobic regions of the gel is substantially lower than that in the hydrophilic regions. It was concluded that the hydrophobic and hydrophilic regions and the local dynamics of them dictate practical application of the polymer associative systems.
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1. Introduction

Considerable recent attention has been focused on the properties of the self-associating polymers and their aqueous solutions [1]. The interest is primarily due to the prospects of the practical uses such as an improvement of the efficiency of the oil recovery, dye production, in biotechnology and pharmaceutical industry, etc. [2,3].

In the present work, the self-associating polymer systems were investigated by the spin probe technique. The main goal of the work was to determine the local dynamics since the local dynamics and local organization of the systems are expected to determine their physicochemical properties and practical applications.

The list of polymers studied includes:

1. hydrogels created by hydrophobically modified polymers;
2. aqueous solutions of polymeric micelles created by block copolymers of hydrophobic and hydrophilic units;
3. hydrogels based on poly(acrylic acid) and macrodiisocyanates.

2. Hydrogels of hydrophobically modified polymers

If hydrophilic macromolecules contain a small amount of side or terminal hydrophobic groups, they become capable of self-association in aqueous solutions. As a result the polymeric micelles are formed. The properties of these micelles are greatly different from those of the low molecular surfactants micelles [4] and of the polymeric micelles composed of block copolymers containing hydrophilic and hydrophobic blocks [5]. Self-association of hydrophobically modified poly-

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mers takes place even in very dilute solutions. The aggregates are formed owing to either intra- or inter-molecular interactions [6,7]. Increase in the concentration of a polymer upwards of 1 wt% results in physical gels. These gels differ from ordinary physical gels, such as aqueous gels of gelatin or polyvinyl alcohol, in their high (practically instantaneous) formation rate upon reaching a certain concentration of the polymer in the solution [8]. The high rate of gelation is quite explainable since the junctions of the gels network are already present in the solution, and no time is required for preliminary association of macromolecules. A junction of the gel of hydrophobically modified polymer is shown in Fig. 1.

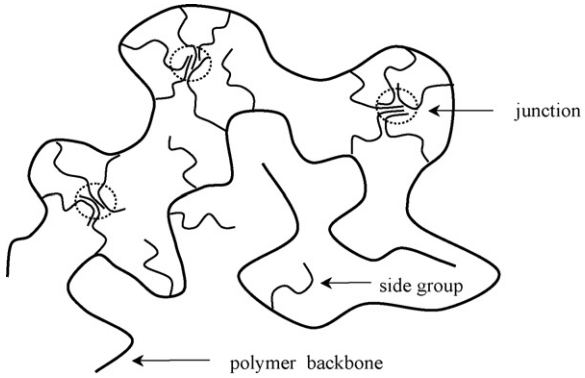
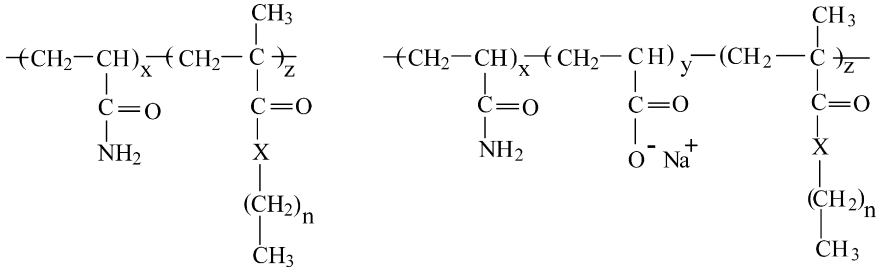


Fig. 1. Schematic image of the gel network junction created by hydrophobically modified polymers.

One of the polymers capable of formation of the physical gels is the modified polyacrylamide. The rheological properties of this gel depend on concentration of macromolecules in solutions, on the length and number of side hydrophobic groups, on the mode of attachment of the hydrophobic groups to the polymer backbone (for example, by means of the ester or amide group), and on the distribution of the hydrophobic groups over a macromolecule [9]. The latter is characterized by a degree of blockiness N_h. The larger the value of N_h, the larger the number of hydrophobic groups located near each other and forming a block [2,9]. The structure of block influences on the strength and stiffness of the gel [8].

An important characteristic determining the physical properties of gels is the local mobility of network junctions formed by hydrophobic groups.

The structures of binary and triple hydrophobic-modified copolymers investigated are presented below. Binary copolymers were synthesized from acrylamide and hydrophobic-modified acrylamide (so-called amide copolymers) or from acrylamide and hydrophobic-modified methacrylate (ester copolymers). In addition to the acrylamide groups and modified monomers, triple copolymers include ionic monomers. Number of alkyl and charged groups in copolymer depends upon conditions of synthesis [10].



Here X = NH (amide copolymer) or X = O (ester copolymer), $n = 8$ or 11. Modified polyacrylamides contain 0.5–1.5 mol.% of side alkyl groups of 9 (C9) or 12 (C12) carbon atoms. Triple copolymer polymer can contain up to 30 mol.% of charged side groups.

The characteristics of polymers used are listed in Table 1.

Having determined the local mobility in gel network junctions one can find out if the mobility depends on the length of side alkyl groups, on the mode of attachment of these groups to the backbone of macromolecules and on the degree of macromolecule blockiness.

Table 1
The characteristics of hydrophobically modified polyacrylamides

The sample no.	Polymer	The content of side hydrophobic groups in polymer (mol.%)	The content of sodium acrylate (mol.%)	$M_w \times 10^{-6}$
1	Ester	0.4 C12	–	0.25
2	Amide 1	1.0 C12	–	0.10
3	Amide 2	1.0 C12	–	0.13
4	Amide 3	1.5 C9	–	1.29
5	Amide 4	0.5 C9	–	1.65
6	Amide 5	1.5 C9	10	0.88
7	Amide 6	1.5 C9	20	1.30
8	Amide 7	1.5 C9	30	1.23

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