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Molecular weight effect on swelling of polymer gels in homopolymer solutions: a fluorescence study

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Abstract

A novel technique based on in situ steady state fluorescence measurements is introduced for studying swelling processes of gels formed by free radical crosslinking copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM) in homopolymer solutions. Gels were prepared at 55 ± 2 °C for various EGDM contents. After drying these gels, swelling experiments were performed in chloroform solution of anthracene labeled poly(methyl methacrylate) (An-PMMA) in various molecular weights at room temperature by real time monitoring of anthracene fluorescence intensity. Anthracene labeled PMMA chains having various molecular weights were prepared by atom transfer radical polymerization at 90 °C. During the swelling experiments, it was observed that anthracene emission intensities increased due to trapping of An-PMMA chains into the gel as the swelling time is increased. The trapping of An-PMMA chains in swollen gel, increase by obeying parabolic law in time. Penetration time constant, τ of PMMA chains were measured and found to be increased as the crosslinker density of gel is increased. It is observed that τ values are much higher for high molecular weight An-PMMA chains than low molecular weight chains in all gel samples. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Investigation of phase equilibrium in ternary systems involving crosslinked gel, a linear polymer and a solvent has been of interests for many years. In general swelling of crosslinked polymer network by mobile polymer chains in solvent can be interpreted by Flory–Rehner theory [1]. It has been found that the Flory–Huggins interaction parameter for the pure swollen network is usually much larger than in the corresponding uncrosslinked system. A swollen polymeric gel immersed in the solution of a linear polymer shrinks as the concentration of the linear polymer increases because of reduction in effective solvent quality of the polymer solution [2]. Bastide et al. studied the volume change of polystyrene gel in toluene solution of mobile polystyrene at high and low concentrations and interpreted the shrinking behavior of the gels on the basis of scaling concepts [3]. An equation of state for ternary systems was derived [4] by means of which the interaction parameter can be deduced. Partitioning of the mobile polymer chains between the solution and the gel was studied to understand the effect of the molecular mass on the partition coefficient [5]. Concentration dependent collapse of single chains in the semi-dilute solution of incompatible polymer was studied theoretically [6] and experimentally [7]. For a long time, common belief has been that the mobile chains do not penetrate into gel, even if they are compatible with the crosslinked chains. Experimentally it is hard to discriminate between a thermodynamic and a kinetic behavior. However in all cases, the chains reptate only slowly inside the gel. Brochard studied the partition phenomenon based on the extended Flory model and the scaling theory where three different regimes were distinguished [8].

The equilibrium swelling of gels in pure solvents have been extensively studied [9–11]. The swelling kinetics of chemically crosslinked gels can be understood by considering the osmotic pressure versus the restraining force [12–16]. The total free energy of a chemical gel consists of bulk and shear energies. In fact, in a swollen gel bulk energy can be characterized by the osmotic bulk modulus K, which is defined in terms of the swelling pressure and the volume fraction of polymer at a given temperature. On the other hand the shear energy which keeps the gel in shape can be characterized by shear modulus G. Here shear energy

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