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Dynamics of Entangled Polymers

MICHAEL RUBINSTEIN, University of North Carolina

The effect of entanglements on polymer dynamics is one of the most interesting and most challenging areas of polymer physics. In 1967 Edwards introduced the confining tube model for polymer networks in which the effect of permanent entanglements from surrounding chains on a given one was replaced by the confining tube potential. In 1971 de Gennes proposed reptation model, suggesting that entangled chains diffuse along their confining tubes. This ingenious idea provided a simple explanation for strong molecular weight dependence of relaxation time and self-diffusion coefficient of entangled linear polymers. In 1975 de Gennes put forward the concept of constraint release that takes into account modifications of the confining tube caused by the motion of surrounding chains forming this tube. In the same paper de Gennes showed that dynamics of entangled branched polymers, such as stars, is qualitatively different from that of entangled linear polymers. Branch points do not allow these molecules to reptate along their confining tubes, as linear molecules do, but instead stars can only relax and move by a highly entropically unfavorable process of arm retraction. I will describe the development and modification of ideas put forward in de Gennes' original models of dynamics of entangled linear and branched polymers. Some details of de Gennes' constraint release model were modified and the concept of tube dilation was introduced couple of years later. For the following quarter of century scientists are debating whether constraint release or tube dilation is the dominant mechanism for relaxation of branched and linear polymers. The shape of the entropic potential for the arm retraction mechanism of branched polymers proposed by de Gennes was modified by Doi and Kuzuu in 1980. This potential is acting along the primitive path – the axis of the confining tube, and the resulting relaxation time of the branched polymers strongly depends on the precise definition of this primitive path. Unfortunately, the primitive path is still not clearly defined by any of the existing models and scientists are still arguing which definition is better. I will describe these and other challenges and open questions remaining in the field of entangled polymer dynamics.