

# Physical Crosslinking of Aqueous Polymer Dispersions: A Perspective

Nicholas Ballard,\* Nerea Jimenez, and José M. Asua

Colloidal polymers, and in particular aqueous polymer dispersions, are widely used in commercial applications such as coatings and adhesives. Historically, the solvent resistance and mechanical properties of these systems have been improved by covalently crosslinking the polymer chains after drying. More recently, work has been directed toward replacing this covalent crosslinking, which typically involves highly reactive functional groups, by physical crosslinking through the use of supramolecular interactions. While conceptually similar to the use of covalent crosslinking, physical crosslinking has a unique influence on the rheology of the polymer, which leads to substantial differences in the development of mechanical strength during drying, as well as the mechanical properties of the final polymer film. In this perspective, the advantages and challenges of this approach are outlined, and an outlook for future research in this direction is provided.

## 1. Introduction

Polymer materials are widely employed as adhesives<sup>[1]</sup> and as coatings for the decoration and protection of substrates.<sup>[2]</sup> Traditionally, solvent-based polymers have been employed, but it is now well established that the high levels of Volatile Organic Compounds (VOCs) in solution polymers, particularly those used in coatings, are a major contributor to environmental pollution,<sup>[3]</sup> which has led to increasingly strict regulations in their use. As the negative impact of VOCs on the environment has become a more important societal issue, films cast from aqueous polymer dispersions, such as acrylic latexes,<sup>[4]</sup> polyurethane dispersions,<sup>[5,6]</sup> and waterborne polyesters,<sup>[7,8]</sup> are increasingly being used in their place.<sup>[9,10]</sup> The use of water as a dispersant leads to low levels of VOCs and improved process sustainability, but the mechanical properties of films cast from waterborne polymers are typically not as good as those of solvent-based polymers. These differences

in mechanical properties arise because of the unique film formation process of polymer latexes, which can lead to poor cohesive strength in films cast from waterborne systems. Thus, solvent-based systems still dominate the market in applications that require high levels of mechanical performance.<sup>[11]</sup>

In commercial formulations, one common approach to improve the performance of waterborne systems is to chemically crosslink the polymer by the formation of irreversible covalent bonds between chains.<sup>[12–14]</sup> The formation of a 3D polymer network enhances the solvent resistance, thermal stability, mechanical performance, and durability of the materials, thus overcoming many of the issues associated with waterborne systems.<sup>[15,16]</sup>

While this approach has been successful, it typically employs highly reactive functional groups that are subject to increasingly strict regulation. Given that a central benefit of the use of polymer dispersions over solvent-based polymers is their improved environmental profile, it would be desirable to limit the use of toxic chemicals for the crosslinking process. In light of this, there has been a substantial amount of work performed recently that has sought to use physical bonding to crosslink the chains in place of covalent bonds.

In this perspective, we first outline the various physical interactions that have been used in supramolecular polymerization systems and the unique influence they have on the rheological profile of polymers. The influence of the change in the rheological profile of physically crosslinked polymers is then discussed in the context of film-forming dispersions, highlighting in particular differences in the film-formation process as well as in the mechanical properties. Finally, we outline strategies that have been used to physically crosslink polymer dispersions and their potential use in coatings and adhesive applications.

## 2. The Chemistry of Physical Crosslinking

There are a number of chemistries that can be used to induce physical crosslinking, the majority of which operate on the basis of a simple reversible association through physical bonding.<sup>[17–21]</sup> In that case, the parameter that expresses the complexation state of the functional groups in equilibrium is the equilibrium association constant ( $K_a$ ), which is defined as the ratio between the concentration of the associated dimer and the product of the concentrations of the free groups in equilibrium. Of the various systems

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# Aqueous Polymer Dispersions

**Chao Zhang**



## **Aqueous Polymer Dispersions:**

## Whispering the Secrets of Language: An Psychological Quest through **Aqueous Polymer Dispersions**

In a digitally-driven earth wherever monitors reign great and quick conversation drowns out the subtleties of language, the profound secrets and mental nuances concealed within phrases frequently go unheard. Yet, situated within the pages of **Aqueous Polymer Dispersions** a captivating fictional value blinking with raw thoughts, lies a fantastic journey waiting to be undertaken. Written by a talented wordsmith, that wonderful opus attracts visitors on an introspective trip, softly unraveling the veiled truths and profound influence resonating within the material of each and every word. Within the mental depths of the emotional evaluation, we will embark upon a sincere exploration of the book is primary subjects, dissect their interesting writing fashion, and yield to the strong resonance it evokes strong within the recesses of readers hearts.

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