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Block copolymers for waterborne coatings—A novel eco-friendly approach for improved coating adhesion to untreated polypropylene based plastics

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ABSTRACT

Over the last two decades significant academic research has been devoted to the development of controlled radical polymerization (CRP) techniques for the synthesis of block copolymers. Widespread industrial application of these valuable synthetic tools has been limited so far, mainly due to the inherent disadvantages of the initial CRP techniques. In recent years substantial improvements were made in the application of CRP in heterogeneous aqueous dispersions and now the time seems right to explore the potentials of block copolymers in waterborne coating applications.

This paper will address one of the major challenges that today's coatings industry is facing: obtaining good adhesion of waterborne acrylic binders to very hydrophobic plastic substrates like untreated polypropylene. Current processes and chemistries for adhesion promotion to polypropylene based plastics typically rely on flame treatment and/or the use of costly and environmentally unfriendly chlorinated polyolefins. It will be shown that the use of tailored water-based block copolymers can provide an alternative eco-friendly approach to adhesion promotion.

1. Introduction

One of the main challenges in the development of waterborne acrylics for the plastic coatings industry is to obtain good adhesion to very hydrophobic plastic substrates like untreated polypropylene (PP) based plastics. The difficulty of obtaining good adhesion to polypropylene is related to its very low surface tension, which negatively affects wetting of the coating binder, and to its low polarity, which gives a poor chemical interaction. Current technologies and processes to obtain good coating adhesion to untreated PP based plastics are based on surface treatments and/or the use of adhesion promoters. Surface treatments include chemical and physical methods such as chemical etching, corona discharge and flame treatment. These treatments result in the formation of polar groups on the polymer surface such as pendant hydroxyl, chloro, amino and carboxyl groups, which can provide improved wetting (as the surface tension is increased) and potentially enhanced chemical interaction with the applied coating composition. Such surface pretreating methods however are often labour intensive, non-uniform and moreover reversible. Adhesion promoting additives or primers based on solventborne chlorinated polyolefins (CPOs) are also widely used for attaining good coating adhesion to PP based plastics in the automotive coatings industry. Solventborne CPOs can provide adhesion promotion through improved surface wetting and intermixing (or bonding) with the topcoat [1]. Also the type and amount of solvent can play a crucial role in obtaining adhesion through swelling of the rubber in PP based plastics leading to increased dispersive interactions and/or mechanical interlocking of the CPO with the substrate [2]. It is however well understood that solventborne CPOs are expensive and environmentally unfriendly. Although the development of novel water-based chlorine-free polyolefin adhesion promoters has gained significant interest over the last years, these are often even more expensive and tend to provide poorer adhesion than solventborne CPOs due to reduced degree of penetration in the outer PP based plastic surface layer [3,4]. Furthermore, waterborne polyolefin based adhesion promoters often lack compatibility with common waterborne acrylic or urethane coating binders.

In the past much work has been done on improving adhesion of aqueous acrylic binders to untreated PP based plastics using alternative environmentally friendly approaches. Some polymers have been reported to give a certain level of coating adhesion, but all of these have their specific disadvantages. For example a hydrophobic polymer like poly(isobornyl acrylate) (iBOA) is known to provide adhesion promoting properties to untreated PP [5], most likely through enhanced dispersive forces resulting from chemical similarities of PP and the 7,7-dimethyl norbornanyl group of iBOA. However, polyiBOA is also a very brittle polymer that easily loses adhesion when subjected to mechanical forces. Next to sufficient binder flexibility, the very hydrophobic polyiBOA should also be water-dispersible. Clearly, the development of an iBOA based binder that offers a combination of these desired properties is very

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challenging. In this respect, a block copolymer could offer the clear advantage of combining water-dispersing properties in one block with the unique adhesion promoting properties from the pure iBOA homopolymer in another block. Unfortunately however, widely used industrial polymerization processes such as free-radical emulsion polymerization offer very limited control over polymer chain composition and architecture.

In this paper we highlight the design of water-dispersible iBOA-based block copolymers via a selected controlled radical polymerization technique for adhesion promotion of waterborne acrylics to untreated polypropylene. The importance of polymer design in adhesion of waterborne binders to such hydrophobic plastic substrates is demonstrated by comparing the adhesion performance of the synthesized block copolymers with that of conventional random copolymers and emulsion polymers of comparable overall monomer composition. It is shown that these novel block copolymers can provide significant added value in waterborne coating applications, especially when combined with a conventional industrial polymerization process such as emulsion polymerization.

2. Block copolymers via controlled radical polymerization

With the availability of controlled radical polymerization (CRP) techniques many new opportunities have emerged in the design of functional polymer materials like e.g. block-, graft- and star-shaped copolymers. The best known and most widely studied CRP techniques are stable free radical polymerization (SFRP), most commonly nitroxide mediated polymerization (NMP) [6], atom transfer radical polymerization (ATRP) [7,8] and reversible addition-fragmentation chain transfer (RAFT) polymerization [9–11]. The strength of these CRP techniques lies in the ultimate combination of the desired chain growth control in ionic polymerization with the versatility and robustness of conventional free radical polymerization. Key in CRP is to establish a dynamic equilibrium between active propagating chains and dormant chains that are unable to propagate or terminate, thereby reducing the rate of radical termination per polymer chain.

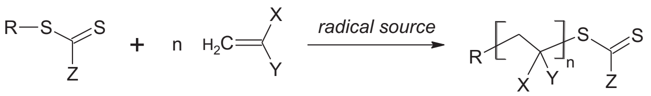

Fig. 1. Overall reaction in RAFT polymerization.

Controlled polymer microstructures like block copolymers have always been of great interest to both academia and industry, and hold much potential for waterborne coatings. To date however CRP techniques have found limited industrial application, which is at least partially due to their specific drawbacks. For example, NMP requires relatively high polymerization temperatures to obtain acceptable reaction rates. ATRP being more versatile and robust relies on the use of relatively high levels of transition metal complexes (mostly copper based) that need to be removed after polymerization. Although significant progress has been made over the last years to reduce the required catalyst level down to ppm levels [12], ATRP remains problematic in combination with protonated acidic monomers commonly applied in emulsion polymerization recipes. RAFT polymerization on the other hand involves the use of special thiocarbonylthio compounds that do allow controlled polymerization of acidic monomers, but can also have a negative impact on the final color and/or odor of the polymer product [13].

Direct application of CRP techniques in heterogeneous aqueous dispersions is known to be rather challenging due to issues related to partitioning of the controlling agent and retaining colloidal stability [14]. Nevertheless, the ability to control the design of waterborne polymers remains very appealing to the coatings industry [15]. Much progress has also been made in recent years to overcome or circumvent the issues of combining CRP techniques with waterborne polymer technologies, as is also seen from the growing amount of published papers and patent applications. Thus far, RAFT polymerization appears most promising for industrial application to waterborne coating technologies given its ease of applicability to existing polymerization recipes and procedures, and given the direct access to water-dispersable block copolymers [16]. The use of pre-designed block copolymers as particle stabilizers for acrylic dispersions is of particular interest as it provides access to a broad range of novel waterborne binders with tunable functionality, without the usual formation of damaging hydrophilic by-products.

The control over polymer chain growth in RAFT polymerization is ensured by thiocarbonylthio [Z–C(=S)–S–R] compounds (RAFT agents) that behave like very active chain transfer agents. Fig. 1 shows the overall RAFT reaction.

RAFT agents can be broadly categorized into four classes, depending on their respective Z-group: dithioesters (Z = aryl or alkyl), trithiocarbonates ($Z = S–R'$), dithiocarbamates ($Z = NR'R''$) and xanthates ($Z = OR'$). At the end of the RAFT polymerization the thiocarbonylthio group remains covalently bonded to the polymer chain end, which could potentially give issues regarding residual color and/or malodor. Although various RAFT end-group removal methodologies are reported in the open literature [17], it seems advisable to carefully select the RAFT agent when making designer polymers for coating applications. For example, xanthates also referred to as MADIX agents [11,18] are much less active and therefore offer less polymerization control than common RAFT agents, but are relatively easily synthesized and tend to exhibit a milder odor and color than the more reactive dithioesters.

3. Block copolymer based emulsion binders via RAFT polymerization [19]

The approach for improving adhesion to untreated PP based plastic substrates using iBOA-based block copolymers involved three steps: (1) synthesis of acrylic acid (AA)–iBOA block copoly-

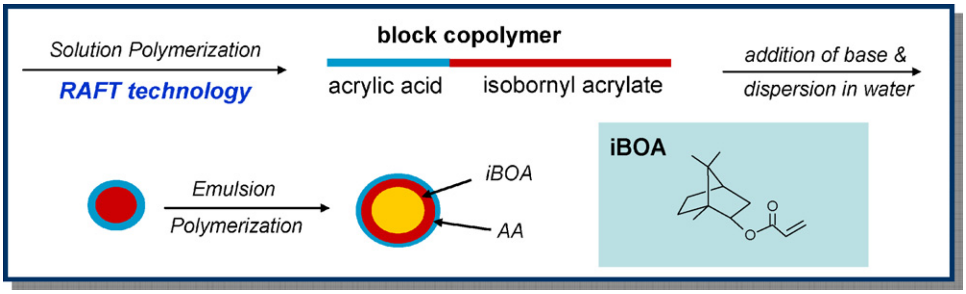

Fig. 2. Approach to an iBOA block copolymer based emulsion binder [19].