

SYNTHESIS AND UTILIZATION OF LOW DISPERSITY ACRYLIC MACROMONOMER AS DISPERSANT FOR NON-AQUEOUS DISPERSION POLYMERIZATION

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Non-aqueous poly(acrylic) dispersions (NADs) used in automotive coating formulations are heterogeneous high-solids suspension of polymeric nano-size particles (< 200 nm) produced by radical polymerization in organic hydrocarbon medium. An important component of the system is the low molecular weight (MW) reactive polymeric dispersant (5000-6000 Da) that stabilizes the particles formed. A vinyl-terminated butyl methacrylate (BMA) macromonomer dispersant synthesized by cobalt chain transfer polymerization (CCTP) has been shown to be more effective at stabilizing the nanoparticles formed during the NAD process than a BMA based grafted dispersant with vinyl groups attached at random positions along the backbone.^[1] The macromonomer, although having controlled double-bond placement through CCT chemistry, still have a molecular weight dispersity of close to two (Figure 1A). While the role of dispersity of a self-assembling amphiphilic block copolymer has been studied in emulsion polymerization,^[2] no such study exists for dispersion polymerization, which commences as a homogeneous solution.

Thus, we have synthesized a low dispersity P(BMA) macromonomer ($\bar{D} < 1.3$, Figure 1B) of similar number-average MW and terminal double bond functionality by sequential application of ATRP and CCTP using bis(difluoroboryldiphenylglyoximate)cobalt(II) [CoPheBF]. Using both methyl acrylate homopolymerization and methyl methacrylate/methyl acrylate (70/30 w/w) copolymerization to produce NADs, the lower dispersity

P(BMA) macromonomer provides better stabilization per dispersant chain, as characterized by smaller average particle size and higher weight fraction of incorporated dispersant (W_{inc}).

We have also synthesized a variant of P(BMA) macromonomer with similar chain length and low dispersity ($\bar{D} < 1.3$), but with modified end-group functionality (Figure 1C) using ATRP and nucleophilic substitution. Unlike Types A and B, the increased reactivity of the Type C end-group allows homopolymerization. However, the synthesis pathway led to a much lower terminal double bond functionality, and thus this variant provided insufficient stabilization to the NAD system.

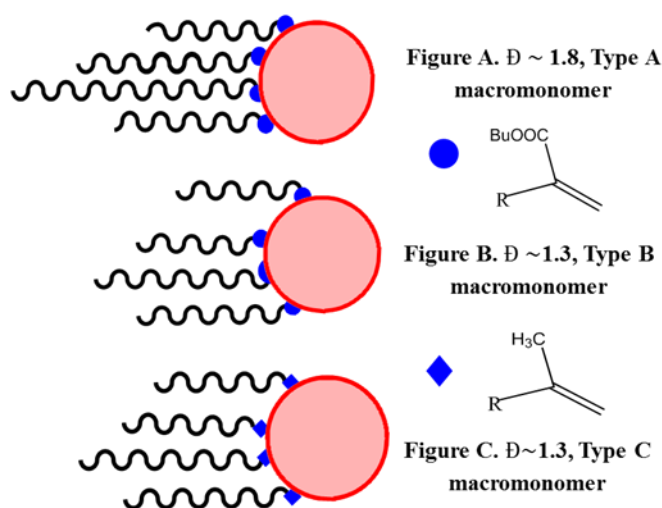


Figure 1. Three P(BMA) macromonomers tested as reactive dispersants in non-aqueous dispersion

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