ELSEVIER

Progress in Organic Coatings 55 (2006) 189–193

PROGRESS IN ORGANIC COATINGS

www.elsevier.com/locate/porgcoat

Molecular weight distribution in living polymerization

Bernd Göbelt

BYK-Chemie GmbH, Abelstrasse 45, 46483 Wesel, Germany

Received 15 June 2005; accepted 27 July 2005

Abstract

An easily obtained parameter for characterizing polymers is the molecular weight distribution (MWD). Polymers with different MWD have different properties. The MWD can be easily influenced with controlled polymerization technologies. Examples of how these methods influence the properties of block and gradient copolymers in wetting and dispersing additives are discussed. These wetting and dispersing additives are used to make solvent-borne paints and aqueous pigment concentrates. An advantage of modulation of the MWD is the ability to fine tune-specific properties, such as the compatibility or the wetting activity of the polymer.

Keywords: Molecular weight distribution; Polymerization; Block copolymers; Gradient copolymers; Wetting and dispersing additives

1. Introduction

Group transfer polymerization (GTP) [1] and the radical polymerization technologies (CRP) atom transfer radical polymerization (ATRP) [2] nitroxyl-mediated polymerization (NMP) [3] and reversible addition–fragmentation chain transfer process (RAFT) [4] are controlled polymerization techniques currently practiced in industry. These techniques are used to customize polymer structures of block and gradient copolymers. The progress of these polymerization technologies focuses on new polymerization mediators or catalysts, to gives advantages like faster polymerization reactions or a more perfect polymer architecture; the polymer characterized by a narrower molecular weight distribution (MWD). Typically, these scientific innovations cannot be fully implemented in industry. Often, there are restrictions in the use of appropriate catalysts and mediators due to notification issues, commercial availability or price of these components. Additionally, industrial production conditions are rarely as perfect as the polymerization conditions in the research laboratory. In production, technical grade raw materials are used without purification. Consequently, polymers with broader molecular weight distributions, meaning less perfect structures are obtained from production than the research laboratory. The broader MWD respective the more imperfect polymer structure are reflected by the properties of the polymer. Further more the different polymerization technologies and the polymerization conditions affect the molecular weight distribution.

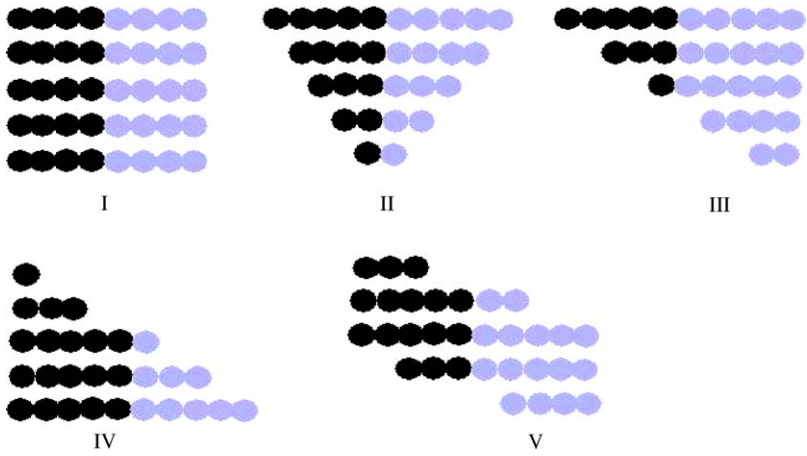
This work illustrates the apparent disadvantage of a broad molecular weight distribution and how these less than perfect polymer structures, can be used advantageously in the design of polymeric wetting and dispersing additives. Examples are given how molecular weight distribution can be used to tune the properties of polymeric wetting and dispersing additives; structure–performance relationships are discussed.

2. Molecular weight distribution

An ideal polymer contains only one type of polymer with the same architecture, microstructure and chain length as shown for the polymer chain composition **I** in Scheme 1. Such a polymer chain composition has a molecular weight distribution of 1.00, as the MWD is a quotient of the weight average molecular weight M_w and the number average molecular weight M_n. In general, the MWD gives a value of the uniformity of the polymer sample. The higher the MWD value, the poorer is the uniformity of the polymer's chain composition. In reality, even with very precise anionic polymerization technologies, a composition of polymeric chains with different chain length is obtained. There are different methods available to analyze the polymer chain composition. For example, size exclusion chromatography (SEC) is a method that is easily used to determine polymer chain compositions. Principally, polymeric chain com-

E-mail address: bernd.goebelt@altanachemie.com.

0300-9440/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2005.07.012



Scheme 1. Different polymer chain compositions.

positions can be divided into the five different types shown in Scheme 1.

Both polymerization technology and reaction conditions can be used to control the polymer chain composition, and with it, the properties of the polymer. In CRP, the polymerization is controlled with an exchange equilibrium; an activation–deactivation equilibrium for ATRP and NMP and an addition–fragmentation equilibrium for RAFT, respectively. The exchange equilibrium depends on the polymerization mediator and the monomer unit, which forms the chain end of the polymer. A change in equilibrium results in a different SEC. To give an example, when the activation rate in the exchange equilibrium becomes slower relative to the rate of chain propagation (monomer addition to the active polymer chain) more monomer units are added before the polymer chain is transferred from its active to its dormant species and consequently, the SEC becomes broader, but still remains symmetrical like composition **II**. The SEC becomes unsymmetrical, when polymer chains stop growing or/and polymer chains are formed during polymerization. In all these cases, a low molecular weight tailing is formed to give an unsymmetrical SEC. Polymer chain composition **III** is obtained by the continuous formation of new polymer chains due to self-initiation of the monomers or addition of an initiator. Its mirror image, polymer chain composition **IV**, results when polymer chains stop growing during the polymerization reaction. When both, chain termination and initiation occur simultaneously, **V** is formed.

It is to be expected that all five different polymer chain compositions **I–V** result in wetting and dispersing additives with different properties.

3. Block copolymers in solvent-based paints

GTP is a polymerization technology to make polymers with very narrow MWD; of polydispersities of 1.10 or less. As GTP is a pseudo-anionic polymerization technique, traces of protic impurities will lead to chain termination reactions and broadening of MWD. Therefore, monomers and solvents must be purified before use. The purification step is the most cost intensive and critical step in GTP, so it is vital to know if a narrow MWD is required for a good wetting and dispersing additive or if a broader MWD can be tolerated. To answer this question, two AB block copolymers with different MWD were compared. The block copolymers are characterized by a first block of different alkyl methacrylates. The second block, containing pigment anchoring groups, is made with methacryloxyethyldimethylbenzylammonium chloride. Block copolymer **1** was synthesized by GTP with a MWD of 1.25. Block copolymer **2** with a MWD of 1.80 was synthesized using a C-RAFT technology. The performance of both wetting and dispersing additives were compared for transparency, gloss and haze of the applied pigmented paints with three different pigments (Table 1).

The paint films of both polymers **1** and **2** with carbon black are comparable, showing negligible differences in gloss and haze values. In paints with Chromophtal red A2B, GTP polymer **1** outperforms C-RAFT polymer **2** expressed by their different haze values. The trend is different for the Heliogen blue which is better stabilized with C-RAFT polymer **2**. This comparison of both polymers and three different pigments shows that each polymer has its strength and limitations regarding pigment selection. The answer to the question if a polymer with a narrow MWD or a broad MWD is a better wetting and dispersing additive is dependent on pigment type and respective paint system. These experiments show that there is no general rule that narrow MWD polymers will outperform broader MWD polymers.

Table 1
Comparison of the block copolymers **1** and **2** Setal 189 XX 65/CAB/Setamine US 138 BB 70

Pigment	Polymer	Transparency	Gloss	Haze
Carbon black FW 200	**1** (GTP)	1	98	42
	2 (C-RAFT)	1	99	72
Chromophtal red A2B	**1**	1	98	99
	2	1	85	202
Heliogen blue L6700F	**1**	2	31	357
	2	1	68	41