Not Your Same Old Polymers:

Same Monomers, New Polymers

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Controlled polymerization techniques provide the chemist with opportunities to customize polymers. The polymers made with these techniques are not only defined by their composition, molecular weight, and polydispersity index, but also by their synthesis method—demonstrated with two AB block copolymer dispersants prepared by GTP and ATRP.

Using these new polymerization techniques, novel polymeric additives for coatings and inks are being developed. Wetting and dispersing additives based on gradient copolymers and leveling additives based on polyacrylate extended polysiloxane block copolymers are two examples of new additive molecules based on controlled polymerization techniques.

CONTROLLED POLYMERIZATION TECHNOLOGIES

Group transfer polymerization (GTP),[1] 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 the industry. These techniques are used to customize polymer structures such as block copolymers. Each of these polymerization techniques has benefits and limitations regarding reaction conditions and monomer range.

GTP is a pseudo-anionic polymerization process. The active polymer chain reacts with monomers via Michael's addition. Other polymerization techniques are controlled radical polymerization techniques (CRP) that position a terminal radical group on the polymer chain as the propagating species. All these controlled radical polymerization techniques are differentiated by their mechanism and reaction conditions;

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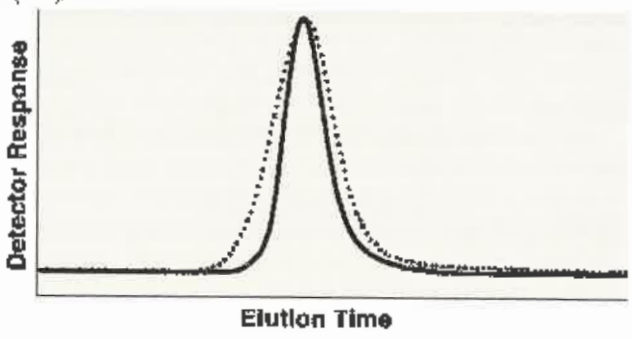
Figure 1—-PC traces of the GTP polymer 1 (—) and the ATRP polymer 2 (•••).



these parameters determine the microstructure of the polymers.

GTP must be carried out in nonprotic media, such as THF with nonprotic methacrylates. When using functional monomers such as methacrylic acid or hydroxyethyl methacrylate, protective groups must be attached for successful synthesis.

In ATRP, the mediator is a halogen atom that is activated by a copper catalyst. As the copper catalyst has a very deep color, it must be removed after the reaction to obtain a colorless product. ATRP is not as limited in monomer range as GTP. Methacrylic, acrylic, and styrenic monomers can be polymerized in ATRP. This technique can tolerate functional groups like hydroxy groups. Acids such as methacrylic acid are challenging, but ATRP systems for these types of monomers are currently being developed.

In NMP, nitroxyl radicals are used as mediators. No purification step is needed in this type of polymerization. NMP accommodates a broad monomer range similar to ATRP. To date, controlled polymerization of pure methacrylate at high conversions is difficult with nitroxyl mediators.

RAFT works with special thio compounds as mediators and is probably the polymerization technique with the broadest monomer range. But its weak point is the synthesis of low molecular weight polymers; it requires relatively longer reaction times for high molecular weight polymers due to retardation.

Table 1—Visual Assessment of the Pigmented Paint: Carbon Black FW 200 200 in a Polyester-Melamine Baking Enamel with CAB 381-2

Additive	Transparency[a]	Gloss R20	Seeds[a]
GTP polymer 1	1	89	2
ATRP polymer 2	4	67	3

[a] 1 = excellent, 5 = poor.

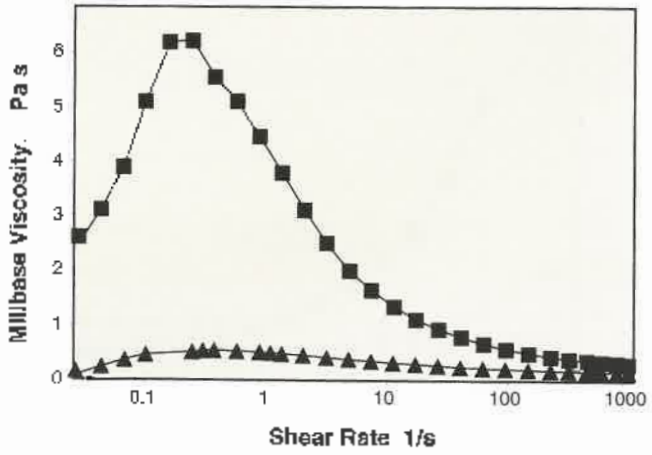
The choice of monomers is not the only criteria for selecting one of these polymerization techniques; monomer distribution along the polymer chains also differs between GTP and CRP, reflecting the differences in propagating species and process conditions.

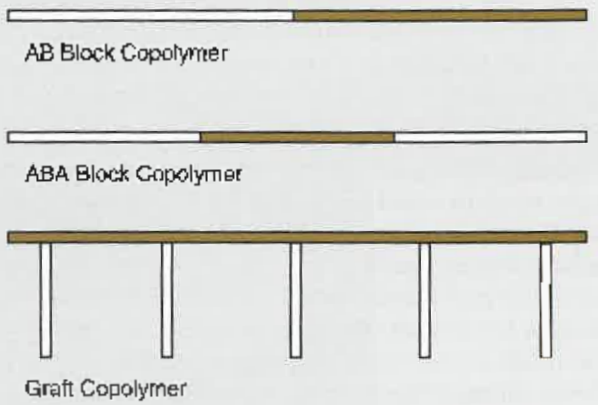
In GTP, the rate of polymerization and temperature in the reaction vessel are controlled by monomer feed rate. The active polymer chain end reacts rapidly with the monomers, resulting in a very low monomer concentration in the reaction vessel. CRP is performed in batch or semi-batch reactions because of its short reaction times; monomer concentration is high and the reactivity ratios of the monomers become important. Even under conditions when the reactivity ratios of the monomers in GTP become important, it is known from literature that GTP and CRP reactivity ratios differ due to different active polymer chain ends.[5]

We can find these differences between GTP and CRP in the properties of wetting and dispersing additives. The properties of two polymers, made using GTP and ATRP, respectively, were compared. The GTP polymer 1 is a commercial BYK product based on an AB block copolymer, where A is a binder compatible block and B is a pigment affinic block based on ionic amine derivatives. The ATRP polymer 2 was synthesized with the same monomer composition and characterization data as the GTP polymer 1 (*Figure 1*). The differences in the performance of polymers 1 and 2 are summarized in *Table* 1 and *Figure* 2. Comparing the rheological performance of both additives in the millbase, the GTP polymer 1 gives a lower millbase viscosity than the ATRP polymer 2. Paints prepared from both millbases show similar differences in transparency, gloss, and seeds.

As the GTP polymer and the ATRP polymer have the same monomer compositions, chain lengths, and simi-

Figure 2—Rheological performance of GTP polymer 1 (■) and its ATRP counterpart, polymer 2 (▲), in the millbase of the carbon black pigment FW 200.





Scheme 1—Block and graft copolymer structures. ❑ = liquid/binder compatible portion and ■ = particle compatible portion (anchoring groups).

lar polydispersity indexes, the different properties of both structures must be the result of different monomer sequences along the polymer chains—reflecting the differences in their synthesis and reactivity ratios of the monomers.

WETTING AND DISPERSING ADDITIVES

Wetting and dispersing additives are typically used to disperse and stabilize pigment particles in liquid media such as paints and solvents. They function as compatibilizers at the solid/liquid interface. Therefore, they must have two different characteristics. In solventborne systems, the binder/liquid-compatible portion of the wetting and dispersing additives are made of either

Figure 3—Rheological performance of the statistical copolymer 3 (■), the gradient copolymer 4 (▲), and the block copolymer 5 (◆) in the millbase of the carbon black pigment FW 200.

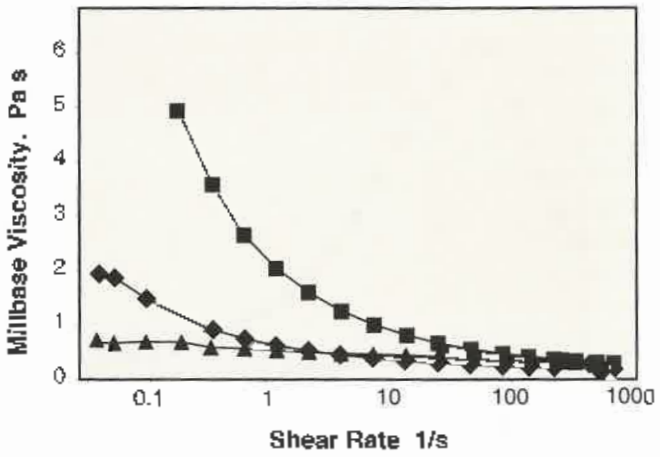


Table 2—Characterization Data of the Polymers 3–5

Polymer	3	4	5
BMA[a]	50%	50%	50%
DMAEMA-BzCl[b]	50%	50%	50%
M_n	9 200 g/mol	6700 g/mol	6800 g/mol
M_w/M_n	2.5	1.4	1.3

(a) BMA: n-butyl methacrylate (liquid/binder compatible).
(b) DMAEMA-BzCl: methacryloyloxyethyldimethylbenzylammonium chloride (anchoring group).

non-polar monomers or polyether-containing monomers, and the pigment-anchoring groups are very often amino derivatives such as tertiary amines, their salts with carboxylic acids or quaternary ammonium derivatives. In aqueous systems, carboxylic acid salts and polyethers are used to provide water solubility of the wetting and dispersing additive; the pigment-anchoring groups are hydrophobic monomers.[6]

These required different characteristics can be obtained with different polymeric structures. State-of-the-art polymeric structures for wetting and dispersing additives are random copolymers, graft copolymers, and block copolymers.[7] Selected block and graft copolymer structures are shown in *Scheme* 1. Both block copolymer structures of the AB and ABA type are easily obtained by using controlled polymerization techniques. Obtaining graft copolymers by two-step techniques are common and controlled polymerization techniques are not necessary.[8]

In random copolymers, the pigment-anchoring areas and liquid/binder-compatible portions are randomly distributed and generally too small to provide strong stabilization effects. In graft copolymers and respective block copolymers, the two different regions are large enough to provide greater stabilization of the particles in dispersion, but the separation of the properties within the polymeric structure causes other drawbacks. These polymeric structures may have a strong tendency to stabilize foam. Micelle formation, mainly due to the incompatibility of the anchoring groups with the liquid medium, can also result in loss of wetting and stabilization activity.

For comparing the structural influence of polymeric wetting and dispersing additives, a random copolymer 3, a gradient copolymer 4, and an AB block copolymer 5 were synthesized using the same monomer composition. Free radical polymerization was used for the random copolymer; the gradient and block copolymers were synthesized with ATRP using a standard protocol published elsewhere.[3] *Table* 2 summarizes the characteristics of polymers 3–5. The performances of polymers 3–5 as wetting and dispersing additives were compared on the basis of millbase viscosity and appearance of their respective pigmented paints.

The millbases contain the wetting and dispersing additive, carbon black pigment FW 200 (Degussa), a polyester resin, and additional solvent. During grinding, foam stabilization was observed with AB block copolymer 5. The viscosity of the millbases is shown in *Figure* 3. The millbase of the statistical copolymer 3 shows high viscosity. Due to the randomly distributed anchoring groups, wetting and dispersing additive 3 acts as a crosslinker between different pigment particles to form a network. The millbase of the gradient copolymer 4 shows a small increase in the viscosity at low shear rates, probably due to some crosslinking; this effect is much less than in the statistical structure of additive 3. At higher shear rates, Newtonian flow behavior is realized for the millbase showing an optimally dispersed and stabilized pigment. Concerning the high viscosity of the millbase with the block copolymer 5, the pigmented paint provides the information for its interpretation. Due to the AB structure of 4, perfect stabilization of the pigment is expected, but the seeds in the paint and the slightly lower transparency of the paint compared to the paint with 4 show that the pigment was insufficiently ground with 5. Larger agglomerates remain in the millbase. As the grinding conditions for all millbases with the additives 3–5 were the same, the conclusion is that the block copolymer is slower to wet the pigment than the polymer structures 3 and 4. The DMAEMA-BzCl anchoring group is a very polar group that is incompatible with non-polar media. Therefore, micelle formation is the most probable cause for the slow wetting behavior of 4. Gloss and haze values as well as the transparency of the pigmented paints with 3–5 can be divided into two groups. The paint with 1 is poor quality, reflecting the poor stabilization of the pigment with 1 in the presence of CAB, which generally leads to pigment flocculation. The paints with 4 and 5 are transparent, with high gloss and low haze values in the same range. The wetting and dispersing additives 4 and 5 are able to stabilize the pigment in the presence of CAB.

For a modern high-performance wetting and dispersing additive, the combination of the benefits of statistical copolymers, which gives fast pigment wetting and low foaming tendency, and block copolymers, which gives good stabilization of the dispersion, is desired. In this comparison, the gradient copolymer structure is the only one that meets all these requirements.

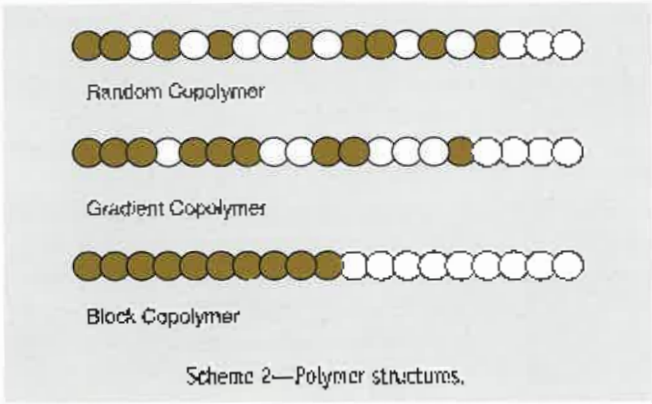
LEVELING ADDITIVES

A smooth paint surface without defects is the goal following the application of paint on a substrate. A less-than-perfect paint surface is the result of localized differences in surface tension —differences between the

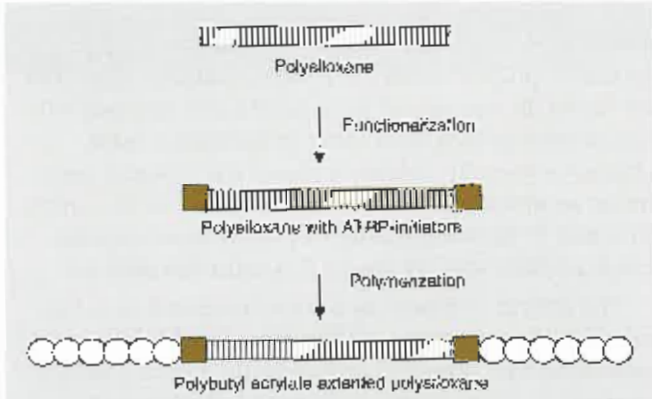
Table 3—Visual Assessment of the Pigmented Paint: Carbon Black FW 200 in a Polyester-Melamine Baking Enamel with CAB 381-2

Additive	Transparency[a]	20° Gloss	Haze	Seeds
3	5	26	465	no
4	1	90	42	no
5	2	93	39	yes

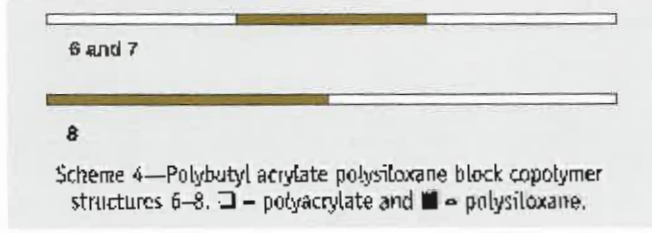
(a) 1 = excellent, 5 = poor.



Scheme 2—Polymer structures.



Scheme 3—Synthesis of polybutyl acrylate polysiloxane block copolymers.



Scheme 4—Polybutyl acrylate polysiloxane block copolymer structures 6–8. ❑ = polyacrylate and ■ = polysiloxane.

Table 4—Assessment of the Different Levelling Additives in an Acrylic-Melamine Baking Enamel

Additive	Amount of Additive	Polysiloxane Content	Film Thickness	Long Wave[a]	Short Wave[a]
9 + 10	0.1 %	20 %	40 µm	3.6	6.2
6	0.1 %	20 %	40 µm	1.0	3.9
7	0.1 %	11 %	40 µm	1.4	3.6
8	0.1 %	11 %	40 µm	1.6	3.2

(a) Wave Scan Byk-Gardner®.

paint and substrate or because of changes in surface tension due to evaporation of solvent or contamination. Leveling additives can be used to adjust the differences in the surface tension as well as provide longer open times for the paint. Leveling additives are mainly based on two chemical classes: polyacrylates, which provide small adjustments in surface tension, and modified polysiloxanes, which can provide large adjustments in surface tension. Unmodified polysiloxanes are usually too incompatible with the paint, resulting in craters. Typically, a physical mixture of modified polysiloxanes and polyacrylates gives better leveling than a polyacrylate- or a polysiloxane-based additive alone, as the mixture covers a wider range of surface tensions than each additive individually.

We report a new concept for leveling additives based on polyacrylate polysiloxane block copolymers.[9] These polymeric hybrid materials are easily obtained with ATRP starting from readily available polysiloxanes. First, hydroxyl groups containing polysiloxanes or modified polysiloxanes were functionalized with ATRP initiators. In the second step, poly(butyl acrylate) side chains were grown from these polysiloxane main chains (*Scheme* 3). *Scheme* 4 shows the different polymeric architectures 6–8, which were used in this study. In 6 and 7, the weight ratio of polysiloxane to polybutyl acrylate was 1:8, in 8, a 1:4 ratio was selected.

The hybrid polymers 6–8 were compared to a 1:1 mixture of two commercially available additives, polyester-modified dimethyl polysiloxane 9, and polybutyl acrylate 10, in an acrylic-melamine baking enamel (*Table* 4). Compared to the mixture of the polyester modified polysiloxane and the polybutyl acrylate, hybrid structure 6, with the same polysiloxane content of 20 wt%, gives a smoother paint surface with better DOI (distinctive of image). Reducing the polysiloxane content similar to polymers 7 and 8 still gives a smoother paint surface than the mixtures of the polyester-modified polysiloxane and the polybutyl acrylate.

SUMMARY

Controlled polymerization technologies can revolutionize the way we look at polymeric additives. No longer can we assume that polymers with the same monomer compositions will provide the same set of performance properties. Two different examples are wetting and dispersing additives and leveling additives based on structured polymers. Wetting and dispersing additives based on gradient copolymers combine rapid pigment wetting with excellent stabilization. Polyacrylate polysiloxane block copolymers give a more superior performance as leveling additives than do mixtures of polyacrylates and polysiloxanes.

Different controlled polymerization techniques are available for the synthesis of tailor-made polymers. Each of these techniques has its own characteristic that partly defines the properties of the polymeric additive. This fact was discussed comparing two wetting and dispersing additives and three leveling additives made with GTP and ATRP.

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