

Synthesis and Characterization of the Copolymer of Dodecyl Methacrylate/Styrene Containing an Amidine Functional Group

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Received 31 July 2000; accepted 25 January 2002

ABSTRACT: A copolymer of dodecyl methacrylate/styrene (DMA/St) containing the amidine functionality was synthesized and characterized. The one-step solution copolymerization process was carried out using a mixed solvent, high temperature, and a functional azo initiator, 2,2'-azobis[*N,N'*-dimethylene isobutyramidine]. Copolymers with different compositions (DMA/St 10/1 to 1/2), molecular weight (M_n , 2000–9000), and functionality (1.0–2.0) were prepared and characterized by NMR, FTIR, DSC, and elemental analysis. The molecular weight of the copolymers could be controlled by the amount of the initiators. Co-

polymer composition depends on the feed molar ratio of comonomers. The amidine functionality of the copolymers was determined by elemental analysis. It was found that 72% of the polymer chain has one functionality. The T_g of the copolymer depends on the feed molar ratio. This copolymer could be used as a potential dispersant for lubricant oil. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1684–1691, 2002

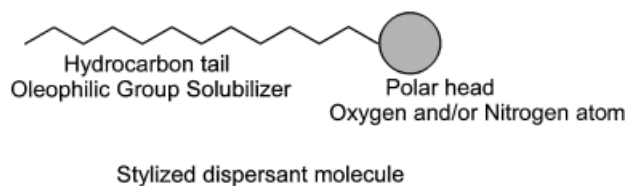
Key words: copolymer; dodecyl methacrylate; styrene; dispersant

INTRODUCTION

Lubricant additives are used to improve the viscosity and performance. Viscosity improvers influence the viscometrics of the oil, especially at elevated temperatures; the performance is improved by so-called additive packages, which control wear and prevent deposit formation.¹ Excessive deposits inhibit mechanical functioning or lubricant flow characteristics. Dispersants are added to lubricants to suspend contaminants and oil-insoluble materials and to prevent deposit formation. They are also used to stabilize emulsions. Their largest application is in crankcase engine lubricants.²

In the 1950s, a new type of additive, a nonmetallic or ashless dispersant, was introduced to help keep engines clean. This product, known as a succinimide dispersant, was a relatively high molecular weight polyisobutenyl group attached to a polar end group. The use of this type of material increased to such an extent that it became the additive component in the highest concentration in pas-

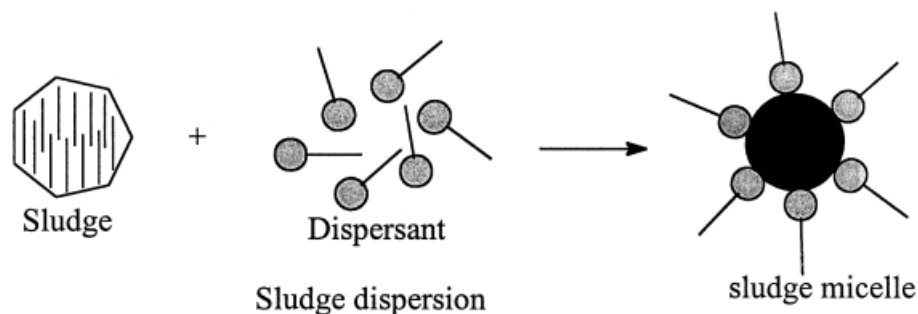
senger car engine oils except for viscosity improvers.³ The following structure shows the stylized structure of an ashless dispersant. The structure of an ashless dispersant is similar to the structure of a surfactant in that the dispersant has a hydrocarbon tail or oleophilic group, which enables the dispersant to be fully soluble in the base oil. The dispersant also has a polar head. The polarity is derived from the inclusion of oxygen, phosphorus, or nitrogen atoms into the molecule:



The sludge and varnish-forming precursors, resulting as a by-product of engine fuel combustion, contaminate the engine oil as they blow by the piston rings into the engine crankcase. Prior to the introduction of dispersants, these contaminants would settle on critical parts of the engine, hampering operation and eventually requiring engine overhaul. Ashless dispersants are designed to have their polar chemical heads attached to rather large hydrocarbon groups. As shown in the following structure, these polar heads interact with sludge particles and the hydrocarbon chain provides the solubilizing action, which maintains the potentially harmful debris in suspension in the oil:

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Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.



The mechanism of the action of those kinds of dispersants were studied by several researchers.³⁻⁶

Engine formulations may contain more than one dispersant to provide optimum performance. For example, one dispersant may excel in low-temperature gasoline engine operation, while another will optimize high-temperature gasoline engine performance. Actually, custom blending the oil with several dispersants would help the product to meet universal oil requirements. Different dispersants have varying effects in interacting with other additives, such as oxidation, wear, and rust inhibitors. In the art of engine oil formulation, these factors have an impact on the choice of dispersant used to maximize engine performance.

Dispersants are nonmetallic or ashless cleaning agents. There are four types of ashless dispersants^{3,7}: (1) succinimides, (2) succinate esters, (3) Mannich types, and (4) phosphorous types. Dispersants are used in a variety of automotive and industrial oils, while combinations of dispersant types are often used in lubricant formulations.

Most dispersants currently in use are prepared from polyisobutylenes ranging in molecular weight from 1000 to 10,000. Their polar functionality arises from amino and/or hydroxyl (alcohol) groups. The contacting groups, in most cases, are either phenols or succinic acids.

Researchers have developed many new types of dispersants over the last 20 years. These include

1. Graft copolymers: The 2-mercapto-1,3,4-triazole moiety grafted to the copolymer of ethylene, a C₃₋₁₂ α -monoolefin, and polyene, reported by Baranski and Migdal in 1998 to be an effective dispersant⁸; a hydrogenated block terpolymer of styrene-ethylene butylene-styrene was grafted by a carboxylic acid anhydride, then followed by imidization with aminothiazadiazole⁹; and a graft copolymer of *N*-vinylpyrrolidone with hydrogenated SBR.¹⁰
2. Polymers of (*N*-3-aminoalkyl)acrylamides and an alkyl acrylate or methacrylate¹¹; selected hydrogenated and functionalized copolymers of a

ring-substituted styrene and a conjugated diene¹²; and poly(1-alkenylamine)s.¹³

3. Reaction products of esters of C₈₋₂₄ olefin unsaturated dicarboxylic anhydride polymers with C₁₀₋₁₈ alkanols reacted with polyamine¹⁴; condensation products of an alkylphenol, paraformaldehyde, and *N,N*-bis(2-hydroxyethyl)-1,3-propanediamine¹⁵; and adducts of alkyl or alkenyl disuccinimides and anhydrides.¹⁶
4. Bicarbamide¹⁷ and bicarbamate.¹⁸
5. Borated reaction products of succinic anhydride, diphenylamine, triethanolamine, and boric acid.¹⁹

Dodecyl copolymers could be used as engine oil viscosity improvers and additive packages.²⁰ The longer hydrocarbon ester side chain makes the copolymer soluble in engine oil. Addition of an amidine functional group into the dodecyl copolymer chain would provide a polar site to suspend harmful soot contaminants. This article describes a one-step free-radical copolymerization of dodecyl methacrylate and styrene containing an amidine functional group on the end of the polymer chain.

EXPERIMENTAL

Materials and their purification

Reagent-grade styrene (St) and dodecyl methacrylate (DMA) were purchased from the Aldrich Chemical Co. (Milwaukee, WI). Passing them through a silicon gel column to remove inhibitors prior to polymerization purified them. 2,2'-Azobis(*N,N'*-dimethylene isobutyramidine) (VA-061) was purchased from Wako Chemical USA, Inc. (Richmond, VA). Toluene, dimethyl sulfoxide, methylene chloride (HPLC grade), methanol (HPLC grade), and tetrahydrofuran were purchased from Aldrich, and they were used as received.

Copolymerization of DMA and St

St (3.64 g, 0.035 mol), DMA (17.8 g, 0.070 mol), a mixed solvent [dimethyl sulfoxide, toluene, total volume (in-

cluding monomers) 300 mL], and VA-061 (1.50 g, 0.006 mol) were poured into a 500-mL three-necked round-bottom flask which was equipped with a magnetic stir bar, a condenser, a nitrogen inlet, and a thermometer. The mixture was stirred at 60°C until all of the initiator was completely dissolved. The temperature was increased to 98–100°C for 24 h. The system became slightly turbid. After cooling, the reaction mixture was transferred to a 500-mL separatory funnel. The separatory funnel was allowed to stand overnight. Two layers were obtained. The top layer was poured into a one-necked round-bottomed flask. The solvents and most nonreacted monomers were removed with a rotary evaporator (100°C/28 mmHg). The resulting product, a viscous liquid, was obtained quantitatively (90%) and purified by dissolving it in methylene chloride, filtering, and removing the solvent.

Characterizations of copolymer

Copolymers were characterized with nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and elemental analysis. ¹H- and ¹³C-NMR spectra were taken in a deuterated chloroform solution using a Bruker ARX 400 NMR instrument. Chemical shifts for the ¹H spectra are in ppm relative to tetramethylsilane and relative to the solvent signal at 77.0 ppm for carbon chemical shifts.

Molecular weight and molecular weight distributions were determined on a GPC system using an HPLC pump Model P4000, an auto sampler AS3000, and an oven SRI Model. Operating conditions were as follows: flow rate, 0.8 mL/min; oven temperature, 40°C; columns, 30 cm and 7.5 mm, PL-Gel 5 μm L-50A, 100A, 500A–1000A; detector, differential refractive index (Model 410, Waters); and injection volume, 100 μL. It was calibrated using narrow-dispersed poly(St) standards.

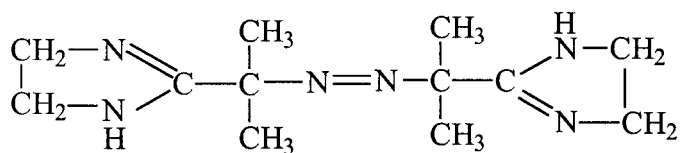
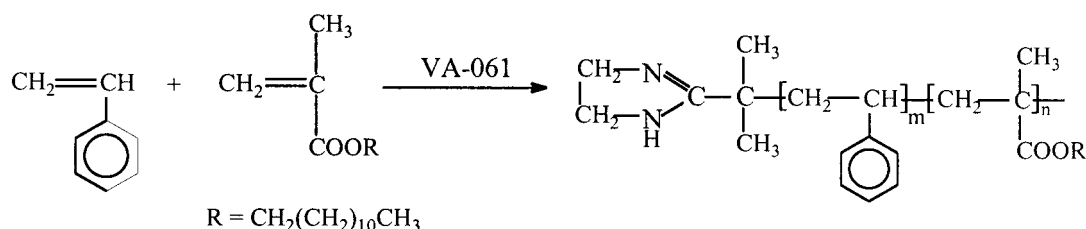
The IR spectra were obtained using a 1750 infrared Fourier transform spectrometer instrument (Perkin-Elmer). Dissolving the polymer in methylene chloride and then forming a thin film on a sodium chloride plate prepared the IR sample.

The glass transition temperatures of the copolymers were determined using DSC 2910 modulated instruments (TA Instruments). The operating conditions were as follows: sample weight, about 5–10 mg, and heating rates, 5°C/min, under a nitrogen atmosphere. Elemental analyses of the copolymers were carried out at the Microanalysis Laboratory at the University of Illinois, Champaign-Urbana.

RESULTS AND DISCUSSION

Copolymerization of DMA and St initiated by VA-061

Polymeric dispersants were synthesized based on copolymers of DMA and St, initiated by an amidine-containing azo initiator VA-061 (see List 1):



2,2'-azobis-[N,N'-dimethylene isobutyramidine](VA-061)

VA-061 is a water-soluble azo initiator. It has found many applications in polymer preparation. Capek et al. reported the dispersion copolymerization of polyoxyethylene macromonomers and St initiated by a water/EtOH soluble VA-061 and oil-soluble benzoyl peroxide.^{21–23} The effects of the initiator type and concentration on the polymer process and kinetics were studied. In the VA-061 systems, the polymeriza-

tion was faster and the molecular weights of the copolymers were greater. Ito and Takatani reported graft polymer production methods using VA-061.^{24,25} VA-061 was treated with methacryloyl chloride (terminally unsaturated hydrogenated acyl compounds). The resulting monomer was polymerized with St and methyl methacrylate to give graft copolymers. Also, graft polymers of vinyl monomers initiated by VA-061

LIST 1
Samples of Copolymers of DMA and St Initiated by VA-061

No	Feed ratio (DMA/St)	M_w	M_n	M_w/M_n	Functionality
C-18	10/1	8000	4900	1.63	—
C-9	10/1	7700	4100	1.89	1.07
C-10	10/1	5500	3800	1.45	1.37
C-19	4/1	9800	5300	1.85	—
C-11	4/1	6100	4000	1.53	1.24
C-12	4/1	4300	3400	1.26	1.43
C-20	2/1	9600	4500	2.13	—
C-13	2/1	5600	3700	1.51	1.18
C-14	2/1	4200	3200	1.31	1.46
C-17	1/1	8200	4100	2.00	—
C-15	1/1	5000	3100	1.61	1.48
C-16	1/1	3700	2700	1.37	1.28
C-21	1/2	6600	3000	2.20	—
C-22	1/4	6300	2600	2.42	—
C-23	0/1 (AIBN)	10,700	6800	1.57	—
C-24	1/0 (AIBN)	41,200	12,400	3.32	—

were introduced onto the surface of aramid powder,²⁶ glutamic acid,²⁷ and carbon black.^{28–30} Narita et al. reported vinyl block copolymers that could be synthesized by a polymerized St-containing azo group, which was polymerized with methyl methacrylate to obtain block copolymers.³¹ Other block copolymers can be made by a similar method.^{32–34} VA-061 can be used to make water-soluble powdered high molecular weight cationic acrylic polymers for flocculants.^{35,36}

A study of these applications of VA-061 reveals that it was used mostly in water or water/EtOH and very polar solvent systems. The aim of this research was the synthesis of an effective novel soot dispersant for lubricant oils based on an amine functional poly(alkyl methacrylate). DMA was chosen as a monomer, the 12 carbon ester of methacrylate providing a high-solubility dispersant in engine oil, and St was chosen as a comonomer to lower the cost. VA-061 was chosen as an initiator. The amidine groups connected to polymer chain ends after copolymerization will bind to acidic soot particle surfaces. For a desirable dispersant, the suitable molecular weights are from 1000 to 10,000.³⁷ Due to the very low T_g [-65°C (ref. 38)] of the DMA polymer, the copolymer of DMA/St with a molecular weight of 1000–10,000 is a very viscous liquid at room temperature.

To prepare such copolymers, the solution-polymerization process is the preferred method. VA-061 is soluble in water, water/EtOH, and methanol and insoluble in common organic solvents. Many different organic solvents for VA-061 were tried. We found dimethyl sulfoxide and toluene to be good solvents for VA-061. The copolymerization process was carried out in the mixture of dimethyl sulfoxide and toluene. At 60°C , the mixed solvent dissolves all the monomers and the initiator and becomes a very clear solution.

Characterizations of copolymer

Structural characterization of copolymer of DMA/St by NMR

$^1\text{H-NMR}$ spectra were used to characterize the structure of the DMA/St copolymers. Figure 1 shows the $^1\text{H-NMR}$ spectrum of the copolymer of DMA and St. The peak assignments of poly(St-co-DMA) by proton NMR are as follows: 6.0–7.2 ppm, broad peak with a shoulder aromatic ^1H of St; 1.9 ppm, methine ^1H of St; 0.2–1.0 ppm, α -methyl ^1H of DMA; 2.7–4.1 ppm, methoxyl ^1H of DMA; 1.0–2.0 ppm, methylene ^1H of DMA and St; and 2.0–2.7 ppm, methylene ^1H of ester of DMA. All the observed $^1\text{H-NMR}$ peaks are broad compared to the homopolymer because the environments change due to tacticity and due to the presence of different

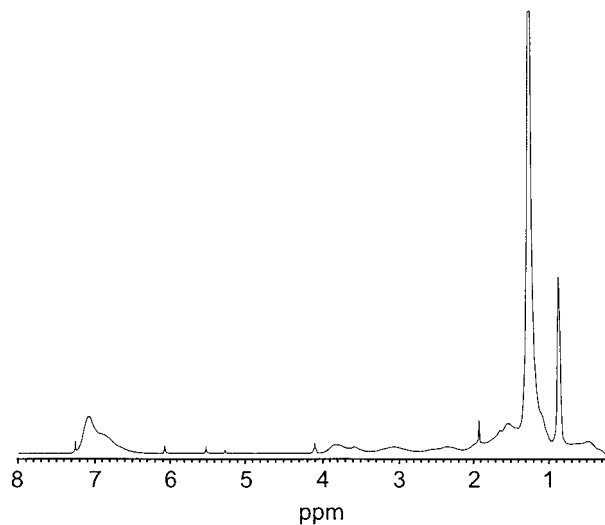


Figure 1 $^1\text{H-NMR}$ spectrum of copolymer of DMA and St.

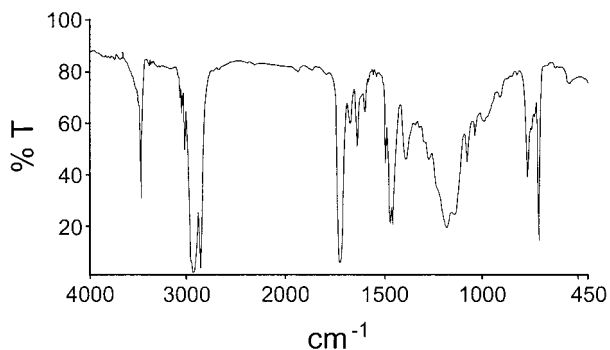


Figure 2 FTIR spectrum of copolymer.

neighbors. Different neighbors result because two DMA units, two St units, or one of each can surround a given DMA unit.

The FTIR spectrum of the copolymer sample is shown in Figure 2. The FTIR spectral assignments are as follows: 3061, 3027 cm^{-1} (Ar—H, stretch), 2922, 2854 cm^{-1} (C—H stretch, —CH₂—, CH₃), 1728 cm^{-1} (—C=O), 1602, 1494 cm^{-1} (aromatic C=C stretch), 1467 cm^{-1} (C—H bending, —CH₂—), 1386 cm^{-1} (C—H bending, —CH₃), and 1180 cm^{-1} (—C—O).

Determination of copolymer composition

NMR spectroscopy was also used to determine the copolymer composition. The proton NMR spectrum for poly(St) shows two peaks at 6–7 ppm, which are characteristics of aromatic hydrogen. These peaks represent four protons and are absent in the proton NMR of poly(DMA). The proton NMR spectrum of poly(DMA) shows a broad peak at 2.7–4.1 ppm, characteristic of the methylene group of the ester that is connected to —OCO groups. This peak represents two protons that are absent in the proton NMR spectrum of poly(St). These two region peaks were used to determine the ratio of DMA units to St units in the copolymers that were produced. The integration ratio gave the composition of the copolymers.

Four series of copolymers were prepared with feed molar ratios of DMA/St of 10:1, 4:1, 2:1, and 1:1. The reactivity ratios for these two monomers are 0.36 and 0.56, respectively.³⁹ Table I shows the resulting copolymer composition and feed molar ratio. Therefore, we can control the copolymer composition of the final products by changing the comonomer feed ratio.

Effect of initiator concentration

For radical chain polymerization, the kinetic chain length is defined as the average number of monomer molecules consumed (polymerized) per radical that initiates a polymer chain. This quantity will obviously be given by the rate of the polymerization to the

initiation rate or to the termination rate since the latter two rates are equal:

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t}$$

Because $R_p = k_p [M] [M\cdot]$ and $R_i = 2kt [M\cdot]^2$, their combination yields

$$\nu = \frac{k_p [M]}{2kt [M\cdot]}$$

which can be combined with $R_p = k_p [M] [M\cdot]$,

$$\nu = \frac{k_p^2 [M]^2}{2kt R_p} \quad (1)$$

For polymerization initiated by the thermal homolysis of an initiator,

$$R_p = K_p [M] \left(\frac{Fkd[I]}{kt} \right)^{0.5}$$

can be substituted into ν to yield

can be substituted into ν to yield

$$\nu = \frac{k_p [M]}{2(fkdkt[I])^{0.5}} = \frac{k_p [M]}{2(fkdkt)^{0.5}} \times \frac{1}{[I]^{0.5}} \quad (2)$$

Equations (1) and (2) show a very significant characteristic of radical chain polymerization. The kinetic chain length is inversely proportional to the radical concentration, polymerization rate, and initiator concentration. The higher the initiator concentration, the lower is the kinetic chain length and, for example, the lower also is the molecular weight.

Effect of the polymerization temperature

The experiments indicate that, with increasing temperature, the average degree of polymerization decreases when a radical initiator initiates polymerization. From eq. (2), assuming $k' = k_p/(kdkt)^{0.5}$, according to the corresponding Arrhenius equation,

TABLE I
Copolymer Composition and Feed Molar Ratio

No.	Feed molar ratio (DMA/St)	Copolymer composition (DMA/St)
C-9	10/1	9.85/1
C-11	4/1	4.06/1
C-20	2/1	2.14/1
C-17	1/1	1.18/1

TABLE II
Molecular Weight of Copolymers of DMA and St

No	Feed ratio (DMA/St)	Initiator (mol % of monomers)	M_w	M_n	M_w/M_n
C-18	10/1	3.0	8000	4900	1.63
C-9	10/1	6.0	7700	4100	1.89
C-10	10/1	10.0	5500	3800	1.45
C-19	4/1	3.0	9800	5300	1.85
C-11	4/1	6.0	6100	4000	1.53
C-12	4/1	10.0	4300	3400	1.26
C-20	2/1	3.0	9600	4500	2.13
C-13	2/1	6.0	5600	3700	1.51
C-14	2/1	10.0	4200	3200	1.31
C-17	1/1	3.0	8200	4100	2.00
C-15	1/1	6.0	5000	3100	1.61
C-16	1/1	10.0	3700	2700	1.37

$$k' = A'e^{-E/RT} = \frac{Ap}{(AdAt)^{0.5}} \exp\{-[(Ep-0.5Et)-0.5Ed]/RT\}$$

$$E' = (Ep - 0.5Et) - 0.5Ed$$

we assume that $Ed = 30$ kcal/mol, $Ep = 7$, and $Et = 4$; hence, $E' \approx -10$ kcal/mol and k' is positive. The value of k' (degree of polymerization) decreases with increasing temperature. For free-radical polymerization, the degree of polymerization can be controlled by the initiator concentration and the polymerization temperature.

Molecular weight of copolymers⁴⁰

For a free-radical copolymerization, the same effect of temperature and initiator concentration can be found. For our dispersants, the desired molecular weight range is from 1000 to 10,000. It is well known that toluene is a

good solvent for solution polymerization and has a significant chain-transfer constant that can help reduce the molecular weight of the polymers formed. So, toluene was chosen as a solvent of copolymerization.

Based on the above considerations, dispersants (copolymers of DMA and St with amine functionality) with the desired molecular weight were prepared using VA-061 as an initiator and toluene as a solvent (actually, using a mixed solvent) at a higher polymerization temperature (98–100°C). Under the above experimental conditions, the molecular weight of the copolymers could be controlled by the quantity of the initiator. Table II shows the results of the copolymerization of DMA and St.

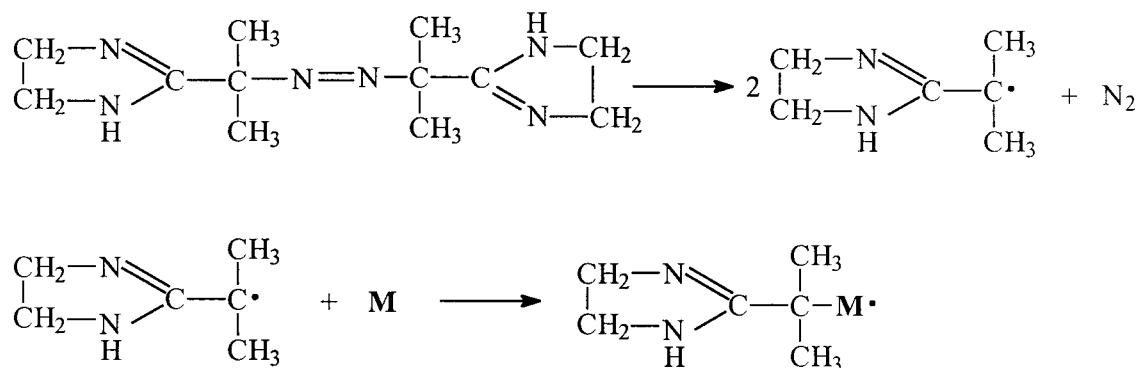
Glass transition temperature of copolymers

For a series of homogeneous copolymers, the T_g values are between the range for the parent homopolymers.⁴¹ From Table III, we can see that the T_g 's of the copolymers lie between the T_g of poly(St) and the T_g of poly(DMA), and there is a very good nonlinear relationship between the T_g and the comonomer feed ratio. We can control the T_g of the final product-copolymers by adjusting the comonomer feed ratio.

Functionality of copolymers

The dispersant has a hydrocarbon tail or oleophilic group, which enables the dispersant to be fully soluble in the base oil and also has a polar head. For the synthesized copolymer, the hydrocarbon tail is the dodecyl ester of methacrylate and the polar head is the amidine group. The functionality of copolymers is the number of amidine group per polymer molecule.

The initiation reaction of VA-061 is the following:



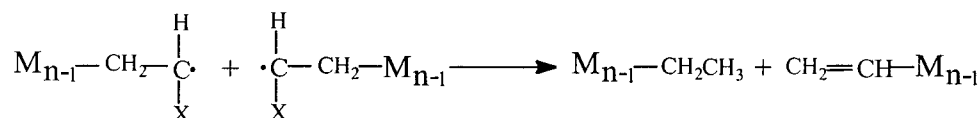
After the decomposition of the initiator, a free radical was obtained. It reacts with a monomer and becomes a monomer radical and starts propagation to form polymer chain radicals. Each polymeric chain radical contains an amidine functionality.

For free-radical polymerization, there are two types of termination mechanisms: combination termination and disproportionation termination.

Termination by combination results in the simultaneous destruction of two radicals by direct coupling:



The degree of polymerization in the two combining radicals can have any value, and the molecular weight of the product will be considerably higher, on average, than that of the radicals so terminated. Termination by disproportionation is when an atom, usually hydrogen, is transferred from one polymer radical to another:



This mode of termination produces a negligible effect on the molecular weight of the reacting species, but it does produce a terminal unsaturation in one of the head polymer molecules.

The measurement of functionality was carried out by elemental analysis. Based on the amount of nitrogen and the molecular weight of the copolymer, the functionality could be determined by multiplying N wt % by the molecular weight and dividing by 28. Table IV presents the elemental analysis results and functionality of copolymers. These results indicate that the amidine functional group does attach to the polymer chain and at least one polymer molecule contains one functional group and some have two functional groups. So, the average functionality should lie between one and two. From the results of functionality, the termination mechanism could be deduced. We assume that disproportionation termination is $X\%$ of the total termination process; the combination termination could be $1 - X\%$. The average functionality is 1.28 (delete the largest and smallest number of functionalities); therefore,

$$1 \times X + 2 \times (1 - X) = 1.28$$

TABLE III
Glass Transition Temperatures of Copolymers

No.	Feed ratio (DMA/St)	Glass transition temperature (°C)
C-24	1/0	-65
C-18	10/1	-55.9
C-19	4/1	-51.5
C-13	2/1	-35.6
C-21	1/2	-13.4
C-22	1/4	7.5
C-23	0/1	.98

TABLE IV
Elemental Analysis and Functionality of Copolymers

No.	% Found			Molecular weight (M_n)	Functionality
	C	H	N		
C-9	74.23	11.23	0.73	4100	1.07
C-10	75.32	11.35	1.01	3800	1.37
C-11	75.86	11.10	0.87	4000	1.24
C-12	73.15	10.77	1.18	3400	1.43
C-13	75.39	10.94	0.89	3700	1.18
C-14	74.81	10.85	1.28	3200	1.46
C-15	77.86	10.74	1.34	3100	1.48
C-16	73.78	10.12	1.33	2700	1.28

After solving this equation, $X = 0.72$ and $1 - X = 0.28$. This result indicates that the disproportionation termination is the major termination process in our system (72% of total termination reaction).

CONCLUSIONS

Copolymers of St and DMA containing the amidine group were synthesized by a free-radical solution polymerization process. They have molecular weights ranging from 2000–9000 and copolymer compositions from 10/1 to 1/2 (DMA/St). Their T_g depends on the copolymer composition. Most of polymer molecules contain one amidine functional group. Their molecular weight could be controlled by the amount of the initiator. Functionality controls and tests of dispersant properties of copolymers are in progress. We will report these results soon.

Sincere thanks are given by the authors to Dr. David Weisleder for the NMR analysis, Mr. Dale W. Ehmke for the GPC analysis, Mrs. Haifa Khoury for the T_g measurement, Mr. Alan C. Lanser for the FTIR spectroscopy, and the Microanalysis Laboratory of The University of Illinois, Champaign-Urbana for the elemental analysis.

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