Novel Cationic Monomers for Inkjet Processes

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Abstract

A new series of monomers have been developed which can be cured cationically by heat or light (radiation). These are very low viscosity (less than 100 cps) and highly reactive monomers with excellent stability at 60°C (catalyzed) compared to present commercially available cationically curable monomers or resins. These unique properties make them ideally suitable for radiation curable inks for high speed ink jet printing processes.

Keywords: Monomers, cationic, low viscosity, inkjet, UV curable

Introduction

There is a growing interest in the inkjet process for industrial (non-graphical) applications. From metal deposition to electronics fabrication to bioengineering, inkjet printing is emerging as the most versatile method for printing, imaging, and spatially controlled liquid deposition that we have ever seen[i].

For UV curing inkjets, a common need, whether using DOD or CIJ technology, are inks which have low viscosity, long pot life, and are fast curing. The primary participant to achieve these objectives is the monomer. The type of monomer chosen is dependent on the curing mechanism involved, either cationic or free radical. Both have their limitations. Typical resins used for cationic curing, which include epoxidized vegetable oils or cycloaliphatic epoxides, have viscosities which are too high for jetting conditions, and must be reduced by volatile solvents to levels as low as 50% total solids. Therefore in most DOD printing applications, the monomers include acrylic esters and urethane (meth)acrylates, which are cured by free radical chemistry. However, these inks require nitrogen blanketing, as oxygen soaks up radicals formed during UV exposure, reducing the efficiency of cure by as much as 80%.

Polyset has developed a new series of multifunctional monomers and oligomers which are cured cationically. These monomers can be viewed as an enabling technology for ink formulators, as they have extremely low viscosity compared to other cationic resins, but at the same time do not exhibit the oxygen inhibition seen with free radical systems. They exhibit low color, low toxicity, high cure speed and high conversion via either heat or light. These materials, based upon a novel siloxane backbone with pendant aliphatic reactive functional groups, form a hybrid inorganic-organic matrix which is ideal for a variety of applications.

Design of Experiment

In order to benchmark the properties of Polyset's novel compositions, we have chosen a pair of commercially available epoxy resins, Dow's ERL 4221, a cycloaliphatic diepoxide monomer, and Arkema's Vikoflex 9010, an epoxidized linseed fatty acid ester. These materials have relatively low viscosity and faster cure speeds, compared to more common BPA epoxy resins or epoxidized vegetable oils. Properties, including viscosity, cure speed, energy requirements, and stability were measured against Polyset materials as described in the Table 1:

Resin	Description
Siloxane Monomer A (SM-A)	Epoxy terminated siloxane
Siloxane Monomer B (SM-B)	Epoxy terminated siloxane
Siloxane Monomer C (SM-C)	Vinyl terminated siloxane
Siloxane Oligomer E (SO-E)	Multifunctional epoxy siloxane

Table 1. Polyset Monomer/Oligomers

Following are some of the results of the experiments:

Resins (Monomer/Oligomer)	Viscosity (cP @ 25°C)
ERL 4221	350 – 450
Vikoflex 9010	60 – 90
Siloxane Monomer A (SM-A)	60 – 90
Siloxane Monomer B (SM-B)	20 – 60
Siloxane Monomer C (SM-C)	20 – 50
Aliphatic Monomer D (AM-D)	10 – 30
Siloxane Oligomer E (SO-E)	3000 – 4000

Table 2. Viscosity of Neat Resins

Polyset monomers have a "head start" when it comes to viscosity. With viscosities ranging from 20-90 cP at room temperature, they are nearly within range of jetting requirements as is, and therefore do not require as much heating in the reservoir or nozzle. This allows a wide variety of blends of materials which are jettable at 60°C, as seen in Figure 1. Also, the incorporation of as little of 10% of a solvent (propylene glycol monomethyl ether acetate, PGMEA for short) results in blends which are jettable at room temperature.

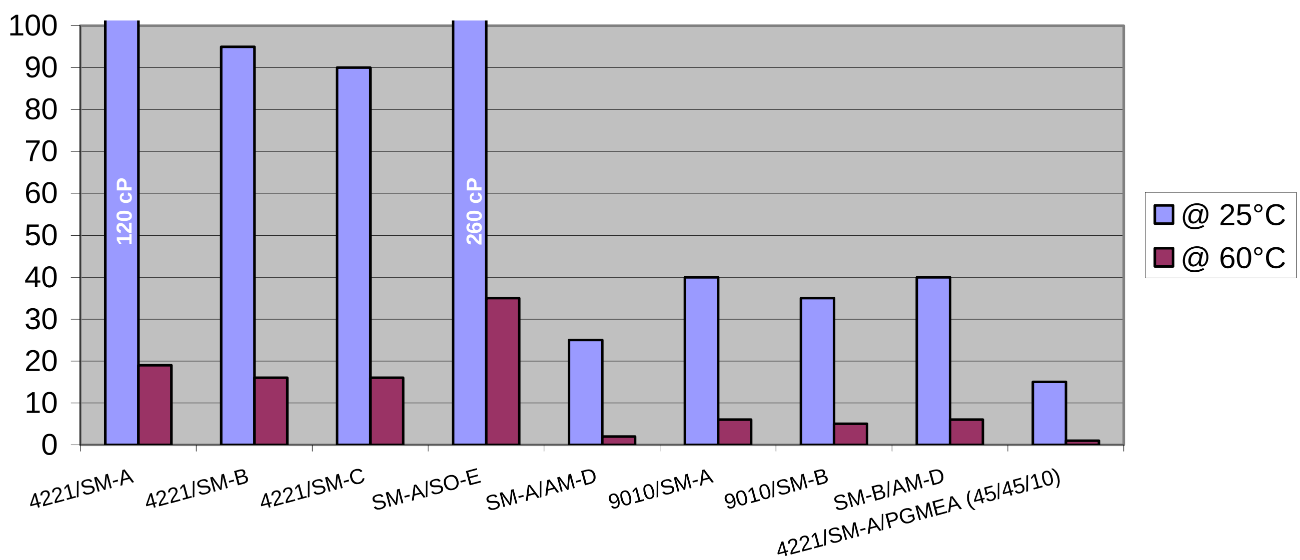

Figure 1. Viscosity of Resin Blends*
(all blends are 50/50 by weight unless noted)

Cure type Catalyst	Gel Pointe* (data in sec) PC-2506	PC-2505	PC-2514
ERL 4221	*1428*	*727*	*1110*
Vikoflex 9010	*931*	*959*	
SM-A	*187*		
SM-B	*137*		
SM-C		*103*	
SM-A/ERL 4221	*818*	*395*	
SM-B/ERL 4221	*800*		
SM-C/ERL 4221	*191*	*383*	*617*
Vikoflex 9010 / SM-A	*511*		
Vikoflex 9010 / SM-B	*570*		
SM-A / AM-D	*212*	*163*	
SM-A / SO-E	*218*		

Table 3. Gel Pointe Data
(see Appendix for Gel Pointe description)

For both Tables 3 & 4, the resins/blends were catalyzed 2% by weight with a series of cationic catalysts. PC-2506 is a diaryliodonium salt which can be both thermally and UV activated. PC-2505 and PC-2514 are mixed triarylsulfonium salts suspended in propylene carbonate and are UV sensitive only. These tables illustrate the speed and efficiency of cure of the siloxane monomers, which are as much as an order of magnitude better than their commercially available counterparts. However, this speed could also be a detriment if the materials are not stable at the jetting temperature, resulting in premature curing in the reservoir, clogged nozzles, and ink droplet deformation.

Catalyst	UV Cure (mJ required) PC-2506	PC-2505	PC-2514
ERL 4221	*1000*	*1000*	*1000*
Vikoflex 9010	*937*	*937*	
SM-A	*< 32*		
SM-B	*< 32*		
SM-C		*< 32*	
SO-E	*< 32*	*< 32*	
SM-A / ERL 4221	*260*	*153*	
SM-B / ERL 4221	*500*		
SM-C / ERL 4221		*81*	*100*
Vikoflex 9010 / SM-A	*39*		
Vikoflex 9010 / SM-B	*200*		
SM-A / AM-D	*< 32*	*< 32*	
SM-B / AM-D	*< 32*		
SM-A / SO-E	*< 32*		

Table 4. UV Energy Requirements

Stability of the ink at jetting temperature is highly dependent upon formulation, especially the additives and photoinitiator used. As mentioned previously, PC-2506 can also be thermally activated, so it would only be suitable for room temperature jetting. However, for the blends using PC-2505, and for the formulations below which also use triarylsulfonium salts, the viscosity can be maintained for up to one week at 60°C.

Table 5,6. Example Pigmented Formulations (White)

Example 1	Pbw
SM-A	38
AM-D	38
Polyol *(Triol)*	8
Byk 30	0.2
White Pigment *(Kronos 2020)*	10
UV Cationic Cat *(50% in P.C.)*	6
Viscosity @ 25C	111
@60C	< 15
With 10% PMA @25C	< 15

Example 2	Pbw
Vikoflex 9010	24
SM-A	12
SM-B	18
BisA Epoxy	5
Byk 307	0.4
White Pigment *(Kronos 2310)*	36.4
Byk 501	0.2
UV Cationic Cat (50% in P.C.)	4
Viscosity @ 25C	96
@60C	< 15

Summary

Up to this point, Polyset has described and demonstrated the properties of a novel set of siloxane monomers which would aid in the industrial inkjet process. These materials share a low viscosity along with a high UV cure speed and efficiency compared to current cationic resins. They also have no oxygen inhibition, and very low toxicity compared to acrylates, which are the current de facto choice for the UV ink monomers. The properties of the cured films are of great interest as well, especially for the printed electronics industry. Key features include:

- Low cure shrinkage, inherent to epoxies
- Broad variety for moduli available – 100MPa to 3GPa, dependent upon formulation
- Low CTE – 50 to 300 ppm, linear from 0 to 200°C
- Excellent thermal stability – up to 300°C for monomers, 400°C for oligomers
- Very low moisture absorption at room temperature or higher – 0.01 to 1%
- Low dielectric, leakage, and low copper ion drift

Polyset welcomes the opportunity to work with inkjet manufacturers and ink formulators to incorporate these novel materials in next generation ink applications.

Appendix

The Gel-Pointe MICROSAMPLE-GELOMETER is a device used in the characterization of UV cured materials. It uses a quartz capillary tube to hold the sample of material being tested while using a small air-pulse pump to move the meniscus past a photocell. When the material is exposed to the UV light the photo cells detects the movement of the meniscus. When the photocell no longer detects movement of the meniscus the timer is stopped and the material is considered gelled.

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[i] Patridge, Stewart. "Bones on Demand: Growing the Skeleton of a New Industrial Inkjet Industry." Screenprinting Magazine 27 May 2005. 12 Jan 2006 <http://www.screenweb.com/index.php/channel/4/id/2249>.