Acryloyl Morpholine for
UV Curing

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Acryloyl morpholine (ACMO) is a reactive monomer capable of undergoing free radical polymerization. Trade literature indicates that it is useful as a reactive diluent in UV-curable formulations[1,2] and its performance has been favorably compared to N-vinyl-2-pyrrolidone (VP).[1] The use of ACMO in radiation-curable formulations, however, has not been widely adopted in the U.S. and little performance data are available.

The structures and physical properties of ACMO and VP are compared in Table 1. ACMO, like VP and most other monofunctional diluents, is a low-viscosity, low-volatility liquid. As homopoylmers, both ACMO and VP form hard, water-soluble polymers.

The goal of current research is to investigate the performance of ACMO in UV-curable systems, gain insight into its reactivity, suggest possible applications, and identify areas for further study.

Toxicological and regulatory information on ACMO is summarized in Table 2 and additional information is available from the supplier.[2] Note that the Toxic Substance Control Act (TSCA) registration of ACMO falls under a SNUR (Significant New Use Rule), which will certainly limit its widespread use in the U.S.

Few reactive diluents display both physical and UV-cure performance properties similar to VP so the possibility that ACMO might be a viable alternative is intriguing. The goal of current research is to investigate the performance of ACMO in UV-curable systems, gain insight into its reactivity, suggest possible applications, and identify areas for further study.

Experimental

Raw Materials

ACMO used in this study was obtained from MIC Specialty Chemicals, Inc. VP and PVP (polyvinyl pyrrolidone, K-30) were obtained from International Specialty Products. Acrylate monomers were obtained from Sartomer Company. Acrylate oligomers were obtained from Cytec. The free radical photoinitiator was obtained from Ciba Specialty Chemicals. The silicone surfactant was obtained from Dow Corning. Methyl ethyl ketone (MEK) and KMnO4 were obtained from Sigma-Aldrich. The polyethylene terephthalate (PET) film used as the substrate, meyer bars, Scotch® brand adhesive tape, and tincture of iodine were all obtained from local vendors.
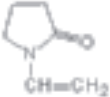
Test Methods

The rate of UV-initiated polymerizations was studied using the Gel-Point I instrument. The oscillation of the liquid formulation in a quartz capillary tube is monitored during UV exposure. At the gel point, oscillations cease and the exposure time is recorded.

The tack-free time of formulations was determined by casting a film of a specified thickness on a polyethylene terephthalate (PET) substrate using a meyer bar. The coated substrate was then exposed to UV light using a Fusion Systems F-300/LC-6 Lab UV Conveyor.

TABLE 1

Physical properties of ACMO and VP

	ACMO	VP
Structure		
Molecular Weight	142	111
Appearance	Clear colorless liquid	Clear Liquid
Odor	Odorless	Characteristic
Melting Point	<-8°C	13°C
Boiling Point	158°C at 50mm Hg	193°C at 400mm Hg
Viscosity	12 cps (25°C)	2 cps (25°C)
Water Solubility @ 25°C	Miscible	Miscible
Tg (glass transition temperature) of homopolymer	145°C	177°C

Tack-free time was defined as the maximum conveyor speed (i.e., minimum UV energy), which will produce a coating that is dry to the touch immediately after UV exposure. UV irradiation intensity measurements were made with the aid of a UVPS Compact Radiometer with sensitivity from 258-480 nm.

Viscosity was determined using a Brookfield Dial Viscometer Model RVT, #4 spindle at 10 rpm.

Coating properties were determined using industry standardized test methods. Adhesion was determined using the crosscut tape test (ASTM D 3359-87). Solvent resistance was determined by rubbing the cured coating with a piece of cheese cloth saturated with methyl ethyl ketone (MEK) wrapped around a 2 lb. ball peen hammer. The number of back and forth rubs ("double rubs") required to break through the coating surface, under pressure applied only by the weight of the hammer, was recorded. Film hardness (ASTM D 3363-74) was

determined by scraping the coating with pencils containing lead with increasing hardness. The hardest lead, which did not break through the coating surface, was recorded. Stain resistance was determined using the spot test (ASTM D-1308). Stains were in contact with the surface for the specified number of minutes and

TABLE 2

Toxicological and regulatory information on ACMO[2]

	ACMO
Acute toxicity	
LD50/oral/rat	588 mg/kg
LD50/dermal/rat	>2000 mg/kg
LD50/inhalation/1h/4h/rat	5.28 mg/1
Local effects	
Eye irratation. Skin irratation, rabbit (OECD 404, 0-8)	0.5
Regulatory Status	TSCA (SNUR)

results reported as 0 = no stain, 5 = severe stain.

Ink receptive coatings were cast on a polyester substrate using a #3 meyer bar, and UV cured at 8 fpm. A test pattern of cyan, magenta, yellow, and red images was printed on the cured surface using an Epson Stylus Photo 700 inkjet printer using standard Epson inks. Dry time was evaluated by touching the ink at 30 second time intervals immediately following printing. Appearance was evaluated subjectively: 0 = high-image quality, 5 = poor-image quality. Water resistance was tested by submerging the printed image under water for 15 seconds and subjectively rating water resistance: 0 = excellent, 5 = poor.

Results and Discussion

Reactivity

The rate of polymerization of ACMO, VP, and TMPTA (trimethylol-propane triacrylate) each containing 3 phr (parts per hundred resin Irgacure 184) [1-hydroxy-cyclohexylphenyl-ketone (HCPK)] was evaluated using the Gel-Pointe I instrument. This technique has been used in the past and found particularly useful in comparing the UV reactivity of different formulations.[3]

It was anticipated that the trifunctional monomer, TMPTA, would gel the fastest due to the high level of crosslinking. However, it was surprising to see that ACMO actually reached its gel point more quickly: less than 25 seconds vs. almost 50 seconds for TMPTA. VP failed to form a gel and the experiment was terminated after 400 seconds. This result was actually expected since, although VP will co-polymerize with acrylates, it does not readily homopolymerize. In fact, the manufacturer recommends use levels of 20-25% weight in order to avoid residual, unreacted VP.[4] To obtain a more accurate comparison of reactivity at the recommended use level, 20% weight of the monofunctional diluents (ACMO and VP) were each blended with 80% weight TMPTA. At this level, the TMPTA/ACMO blend cured faster than TMPTA/VP blend (Figure 1) although the difference was small.

Homopolymer films of ACMO, VP and TMPTA, each containing 3 phr (parts per hundred resin) HCPK, were cast on a polyester substrate using a #40 meyer bar and were exposed to UV light on a conveyorized system. Tack-free times were determined as described in the experimental section. Both ACMO and TMPTA formed tack-free homopolymers films at a conveyor speed of up to 15 fpm (1,000 mJ/cm²). Thinner films, cast using a #3 meyer bar had some surface tack, presumably due to air inhibition. VP, at both coating thicknesses, failed to show any noticeable polymerization. The TMPTA/ACMO and TMPTA/VP blends prepared above were also cast as thin films on a polyester substrate using a #3 meyer bar and were exposed to UV light. Both formulations were tack-free at 15 fpm (Table 3).

The ability of ACMO to readily homopolymerize to this extent is not well understood and will require further investigation. The difference in

FIGURE 1

Gel time of monomers and monomer blends
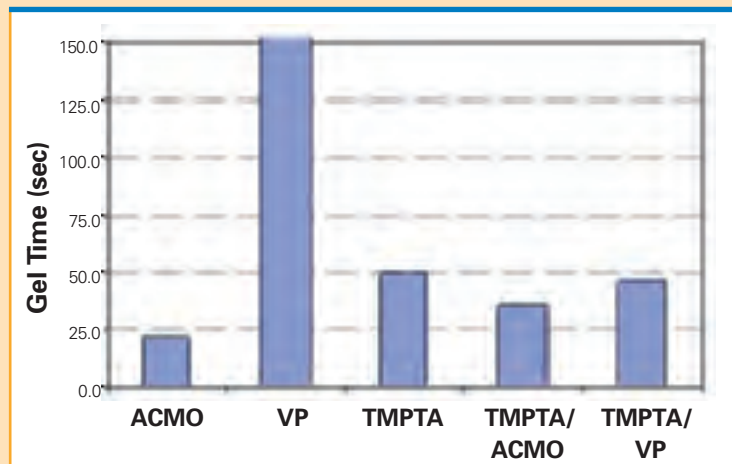
the reactivity between ACMO and VP in copolymerization with acrylates can be best understood by examination of their Q and e values[5] and their reactivity ratios. In the Q-e scheme, Q is the measure of monomer reactivity while e is associated with radical polarity. The Q and e values for ACMO, VP, and a representative acrylate monomer (methyl acrylate, MA) suggest the ACMO will react more like an acrylate than a vinyl lactam (Table 4).

Using this Q-e scheme, reactivity ratios for these monomers were calculated.[8] Results indicate that while ACMO will form an almost ideal random co-polymer with acrylates, VP is incorporated slowly, and will be a minor component of the growing acrylate polymer (Table 5). These data are consistent with the gel-point and cure speed data and help explain why high levels of VP are not recommended.

UV-Curable Formulations

Urethane Acrylate Formulations

The performance of ACMO was compared to VP and EEEA (ethoxy ethoxy ethyl acrylate, a commonly used monofunctional acrylate) as reactive diluents in formulations containing an aromatic urethane acrylate oligomer

TABLE 3

Tack-free time of monomers and monomer blends

Formulation (contains 3 phr HCPK)	Tack-Free Time
ACMO	15 fpm
VP	<15 fpm, wet
TMPTA	15 fpm
ACMO/TMPTA: 20/80 wt.%	15 fpm
VP/TMPTA: 20/80 wt.%	15 fpm

TABLE 4

Q and e values for selected monomers [6, 7]

Monomer	Q	e
ACMO[1]	0.39	0.08
VP[6]	0.088	-1.62
MA[7]	0.42	0.6

TABLE 5

Reactivity ratios for free radical co-polymerization

Monomer 1	Monomer 2	r_1	r_2
MA	ACMO	0.79	0.97
MA	VP	1.26	0.01

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with 20% weight TMPTA (Ebercyl 6700-20T). Diluents were compared at the higher end of the recommended use level for VP (20% weight). In this formulation, ACMO was not as effective as VP or EEEA at reducing viscosity. Films were cast on a polyester substrate using a #3 meyer bar and were exposed to UV light using the Fusion Systems F-300/LC-6 laboratory unit at 8 fpm (1,000 mJ/cm²). Cured films containing ACMO provide solvent resistance and hardness similar to VP and superior to EEEA (Table 6).

Epoxy Acrylate Formulations

The performance of ACMO was also compared to VP, EEEA, and TMPTA as reactive diluents in formulations based on an epoxy acrylate oligomer (Ebercyl 3700). Once again, use levels were at 20% weight. Films were cast on a polyester substrate using a #3 meyer bar and cured as before. Surprisingly, all these formulations exhibited poor adhesion even though VP is reported to provide outstanding adhesion to a wide variety of difficult substrates. [9-12] Unfortunately, this was not pursued further due to a lack of a variety of well-defined substrates. Formulations based on both ACMO and VP were harder than EEEA and equivalent to the more highly crosslinked TMPTA. All formulations had excellent resistance to MEK and were not stained by potassium permanganate. ACMO and VP were slightly stained by iodine, more so than TMPTA but much less than EEEA (Table 7).

Ink Receptive Coatings

Up to this point, the recommended use level has limited the use level of ACMO in formulations for VP (20-25% weight). At only 20% weight, performance differences between ACMO and other diluents may be masked by the other formulation components. This use limitation, however, does not apply to ACMO. It has already shown that, unlike VP, ACMO will readily homopolymerize. Since its homopolymer is water soluble, it is expected that higher use levels will increase the water sensitivity of the film. Note that, unlike ACMO, many UV-curable monomers were developed to create highly solvent (and water) resistant films[13] ("no wax" floor tile coatings, for example). There are some applications, however, where a certain degree of water sensitivity is desired. One such application is UV-curable ink receptive coatings for digital printing and imaging. Ink receptive coatings must retain some

TABLE 6

Urethane acrylate formulations

Formulation (grams)	A	B	C
Urethane acrylate oligomer containing 20% TMPTA	80.0	80.0	80.0
ACMO	20.0		
VP		20.0	
EEEA			20.0
HCPK	5.0	5.0	5.0
Viscosity (cps)	11,100	3,700	2,300
MEK double rubs	131	177	34
Pencil Hardness	HB	HB	B

water sensitivity to allow the inks to dry quickly and maintain a sharp image. This application is currently dominated by solvent-based systems containing 80-90% solvent and cured by IR driers and/or forced air ovens.[14] This seems like an ideal application for UV curing in general, and ACMO in particular.

UV-curable formulations based on ACMO were prepared, coated on a polyester substrate using a #3 meyer bar, and UV cured at 8 fpm. A test pattern of blue, magenta, yellow and red images was then printed on the cured surface using an Epson Stylus Photo 700 ink jet printer. The color image was evaluated for dry time, appearance and water resistance. Ideally, the ink should dry quickly, maintain good image quality and be water resistant.

As a homopolymer, ACMO is ink receptive. Inks dry relatively quickly, but water resistance is poor. Adding PVP (polyvinyl pyrrolidone) increases viscosity improving handling, but has little impact on performance. The effect of various co-monomers on the ACMO/PVP formulation was also evaluated. Adding 17% weight VP

TABLE 7

Epoxy acrylate formulations

Formulation (grams)	D	E	F	G
Epoxy acrylate oligomer	80.0	80.0	80.0	80.0
ACMO	20.0			
VP		20.0		
EEEA			20.0	
TMPTA				20.0
HCPK	3.0	3.0	3.0	3.0
Adhesion	0%	0%	0%	0%
MEK double rubs	>200	>200	>200	>200
Pencil Hardness	6H	6H	HB	6H
Stain Resistance (ASTMD-1308)				
$\quad$ KMnO$_4$ (5 minutes)	0	0	0	0
$\quad$ 2% Iodine Tincture (60 minutes)	2	2	4	1

TABLE 8

Ink receptive coatings

Formulation (grams)	H	I	J	K	L	M
ACMO	100.0	80.0	67.0	67.0	67.0	73.0
PVP-K30		20.0	17.0	17.0	17.0	18.0
VP			17.0			
EEEA				17.0		
TRPGDA					17.0	9.0
HCPK	3.0	3.0	3.0	3.0	3.0	3.0
Surfactant	0.5	0.5	0.5	0.5	0.5	0.5
Dry Time (min)	2	2	1	3	>5	2
Appearance	3*	3*	3*	3*	3*	3*
Water resistance	5	5	5	5	5	5

Mottled appearance with banding

improves dry time, but not water resistance. Adding 17% weight EEEA does not improve water resistance and increases dry time. Adding 17% weight TRPGDA (tripropylene glycol diacrylate) improves water resistance at the expense of dry time. A lower level of TRPGDA improves dry time while maintaining moderate water resistance (Table 8).

Conclusions

ACMO is an effective diluent for UV curing. When compared to VP at typical use levels, it is not as effective at reducing viscosity but is comparable with respect to cure speed, hardness, and solvent and stain resistance. Unlike VP, ACMO can be readily homopolymerized and can be incorporated into acrylate formulations at high levels without adversely effecting cure speed. High levels of ACMO will introduce some water sensitivity to the cured product. This property can be used as an advantage for applications such as ink receptive coatings for digital printing where some coating hydrophilicity is required. Further experimentation is needed to optimize dry time, appearance and water resistance of these coatings. In summary, ACMO is not a "drop in" replacement for VP. It is, however, a unique monomer with its own unique performance and thus provides new formulating possibilities.

Acknowledgements

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