

Oxetanes: Curing Properties in Photo-Cationic Polymerization

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Oxetane Project

Abstract

Novel oxetane monomers are evaluated in a photo-cationic polymerization system. Monomer with p-methoxy-phenyl group on the second position of oxetane ring exhibited high reactivity. In the formulation of oxetanes with cycloaliphatic diepoxide monomer, the viscosity of the formulation was reduced effectively while keeping high surface cure rate as epoxide alone. Difunctional oxetanes exhibited improved solvent resistance.

1 Introduction

In photoinitiated cationic polymerization, many different types of monomers and oligomers have been examined and used [1]. In particular, the photopolymerization of epoxides gives coatings a high thermal capability, excellent adhesion and good chemical resistance. Although photo-polymerized epoxy coatings are known for their high performance, commercially available epoxides, such as bis-phenol-A-diglycidyl ether, undergo photoinitiated cationic polymerization at rather slow rates.

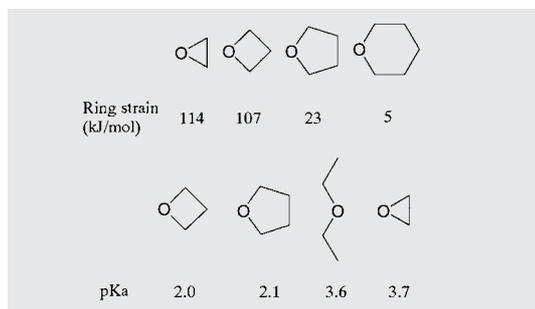
Three major factors contribute to the reactivity of cyclic ethers during cationic ring-opening polymerization [2]. These are basicity, ring strain and steric factors. The basicity and ring strain energy of cyclic ethers are listed in scheme 1. The ring strain of ethylene oxide has been calculated to be 114 kJ/mol while that for oxetane is 107 kJ/mol [3]. At the same time, the pKa for these two ethers is 3.7 and 2.02, respectively [4-5]. Thus, while both cyclic ethers have similar steric factors and ring strains, the basicity of oxetane is considerably greater than that of ethylene oxide. This latter parameter should, therefore, dominate by making oxetanes more reactive than epoxides during photoinitiated cationic ring-opening polymerization.

Previously, the curing property of oxetane monomer in photoinitiated cationic polymerization was investigated in comparison with epoxy monomer [6]. Through real time FT-IR

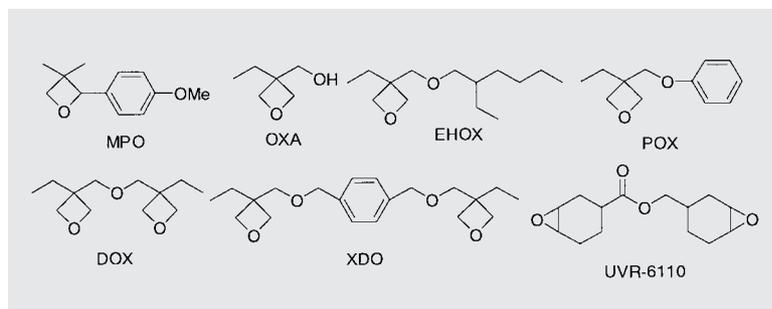
measurements, the oxetane monomer was proved to possess polymerization characters different from those of epoxides toward photoinitiated cationic polymerization. Although rather long induction period compared with epoxide was seen in the early stage of oxetane polymerization, after that stage, polymerization underwent smoothly until high conversion of monomer. In the formulation with epoxy monomers, oxetane exhibited fairly fast polymerization. Computational studies explained the acceleration mechanism of oxetane polymerization to be the fast initiation of epoxide through SN1 ring opening of oxirane ring.

To enhance the reactivity of oxetane in the initiation stage, introduction of electron donating group in the second position of oxetane ring, which results in the formation of stable secondary carbocation intermediate, might be effective for the SN1 ring opening. Based on the above investigation, 3,3-dimethyl-2-(p-methoxy-phenyl)-oxetane(MPO) was selected and the reactivity of the monomer was studied. This paper details the evaluation of MPO toward photo-cationic polymerization using photo-DSC.

As shown so far, the high reactivity of oxetane monomers seems attractive. In this paper, five oxetane monomers (scheme 2) were selected and the performance of their formulation with cycloaliphatic diepoxide monomer in the UV cationic cure was evaluated.



Scheme 1 : Ring-strains and Basicities of Cyclic Ethers



Scheme 2 : Monomers used in this study

2 Experimental

2.1. Raw Materials

The oxetane monomers used throughout this study were synthesized from OXA (DOX, XDO) or 3-ethyl-3-chloromethyl-oxetane (EHOX, POX, DOX) through phase-transfer reaction. MPO was synthesized from 1-(4-methoxyphenyl)-2, 2-dimethyl-1, 3-propanediol according to the procedures of Xianming and Kellogg [7]. Cycloaliphatic diepoxide monomer (UVR-6110) and sulfonium salt cationic photoinitiator (UVI-6990) used in the formulation were obtained from Union Carbide Co.

2.2. Sample formulations

The formulations were prepared by mixing the monomers with UVI-6990 in amber vials. The viscosity of monomers and their formulations was measured at 25°C using Brookfield viscometer. The surface tension of EHOX and the formulations with UVR-6110 were measured at 20°C.

2.3. Photo-DSC measurement

Heat of polymerization during photo-cationic polymerization was measured by DSC220C (Seiko Instruments Inc.) equipped with a UV-1 lighting unit (200W Hg-Xe lamp, Seiko Instruments Inc.). Typical values for light intensity were 11 to 90 mW/cm² at 365nm.

2.4. Curing Test Methods

A uniform coating of desired coating thickness was applied to a test panel using a #3 bar applicator. The liquid coating was cured with a 80 W/cm of high pressure Hg lamp.

Surface Cure Rate (S.C.R.) is defined as maximum conveyor speed which can be used to produce a coating that becomes dry to the touch immediately after UV exposure.

Samples for the evaluation of adhesion, flexibility and acetone resistance were cured using a UV irradiator at 10m/min. of conveyor speed. Polycarbonate (PC), tin free steel (TFS), polymethylmethacrylate (PMMA) and glass were used as test panels for adhesion and TFS for flexibility. Measurement of adhesion and flexibility of cured samples was performed according to the procedures of JIS K-5400. The acetone resistance of the coatings was defined as the maximum number of rubs with a cotton ball impregnated with acetone until the coating starts to be destroyed.

3 Results

Typical properties of oxetane monomers are listed in Table 1. EHOX, possessing long alkyl side chain, showed the lowest viscosity and specific gravity. The slightly high viscosity of OXA

can be explained by the hydrogen bonding of hydroxy methyl groups in the molecule. The simplest di-functional monomer, DOX, exhibited rather low viscosity and specific gravity compared with XDO with xylene moiety in the molecule. Each of the monomers was found to be completely miscible with UVR-6110 at any ratio. All the monomers listed were AMES Test negative. EHOX exhibited low surface tension caused by the alkyl side chains. In the formulation with UVR-6110, the surface tension of the formulation was reduced effectively (Figure 1).

The heat of polymerization of XDO and UVR-6110 was

Table 1 Typical Properties of Oxetane Monomers

Monomers	Viscosity cps @ 25°C	Specific Gravity @ 25°C	Compatibility with UVR-6110	AMES Test
OXA	22	1.024	OK	Negative
POX	14	1.046	OK	Negative
EHOX	4	0.899	OK	Negative
DOX	13	0.999	OK	Negative
XDO	150-170	1.068	OK	Negative

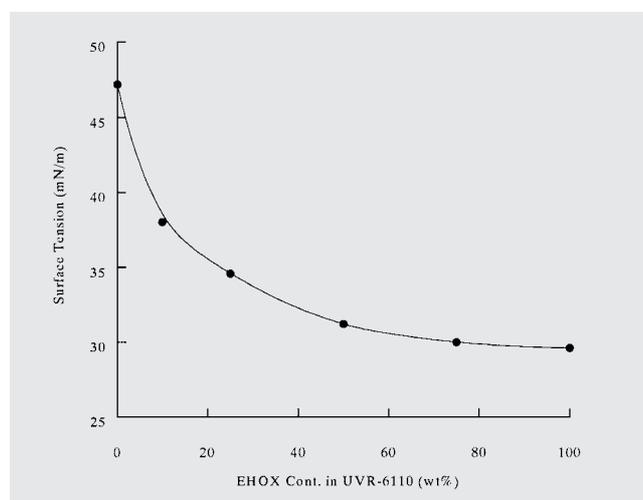


Figure 1. Surface Tension values versus EHOX content in UVR-6110 formulations (at 20 °C)

measured by Photo-DSC and the results are shown in Figure 2. In the photo-cationic polymerization of XDO, higher amount of exotherm was measured compared with that of UVR-6110 in the early stage of irradiation (10 to 30 sec.) and decreased smoothly after the peak (30 to 80 sec.). This smooth decrease could be explained by the fast propagation rate because of the high basicity of oxetane ring. Small amount of heat was seen for UVR-6110 and the heat generation lasted for long during the irradiation (until 10min.). This long heat flow could be explained by the slow polymerization of oxirane ring. With addition of 30 wt% of UVR-6110 to XDO, the induction period of polymerization was shortened showing fast initiation reaction. The heat flow for the formulation lasted long (after 30 sec.) compared with that for XDO alone, showing the polymerization of remaining epoxide.

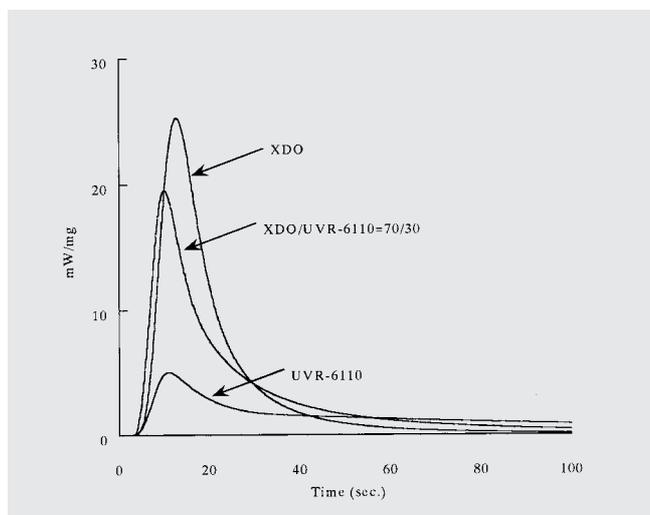


Figure 2. Photo-DSC exo-therm curves for XDO and UVR-6110 formulations ($I=20.0\text{mW/cm}^2$ at 365nm, 3parts of UVI-6990, 40)

The heat of polymerization of MPO and POX with 1wt% of sulfonium salt photoinitiator (UVI-6990) were measured by Photo-DSC and the results are shown in Figure 3. In the photo-cationic polymerization of MPO, sharper exotherm curve was measured compared with that of POX. This higher reactivity of MPO toward cationic polymerization might be explained by faster ring-opening during the initiation stage, which is caused by stable benzyl-type carbocation intermediate. With addition of 10 or 20 wt% of MPO to POX, exotherm curves changed to narrower uni-modal shapes. If the polymerization of MPO and POX proceeded separately, the exotherm curve should be bi-modal. These uni-modal curves indicate that the polymerization of these two monomers underwent co-polymerization and the sharper curves exhibit accelerated polymerization of oxetane rings in POX.

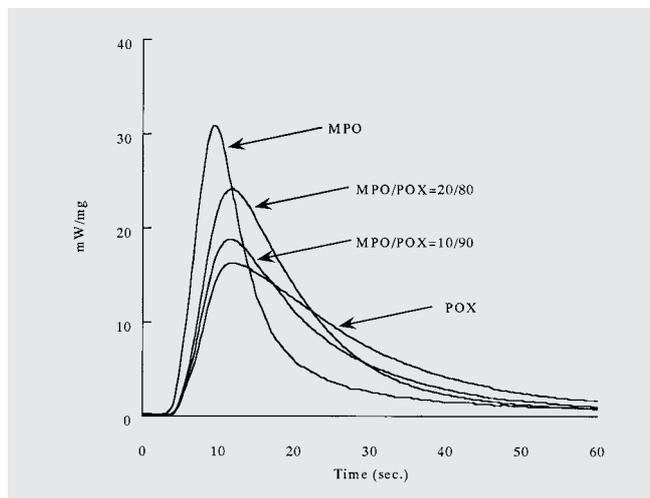


Figure 3. Photo-DSC for POX, MPO and their formulations ($I=11.2\text{mW/cm}^2$ at 365nm) with 1wt% of UVI-6990

The properties of OXA formulations with UVR-6110 were shown in Table 2. The viscosity of the formulation exhibited a decrease as the amount of monomer was increased and, with addition of 15 wt.% of OXA, it reached almost half. The adhesion to PC

Table 2 Formulations of OXA withUVR-6110¹⁾

UVR-6110 ¹⁾	100	95	90	85	80	
OXA		5	10	15	20	
UVI-6990 ¹⁾	3	3	3	3	3	
Viscosity(cps) ²⁾	375	266	214	170	138	
S.C.R.(mpm) ³⁾	20	>50	>50	>50	30	
Adhesion ⁴⁾	PC	OK	OK	OK	NG	NG
	Steel	OK	OK	OK	OK	OK
	PMMA	NG	NG	NG	NG	NG
	Glass	OK	OK	OK	NG	NG
Flexibility ⁴⁾	8mm	NG	NG	NG	OK	OK
	6mm	NG	NG	NG	OK	OK
	4mm	NG	NG	NG	NG	OK
	2mm	NG	NG	NG	NG	NG

1) Union Carbide
2) Measured at 25°C
3) S.C.R.; Surface Cure Rate. Coatings applied to steel panel with a #3 bar and cured with 80W/cm² high pressure Hg lamp at varied conveyor speed (mpm; meter per minute)
4) Measured according to JIS K-5400. Coatings applied with a #3 bar and cured with 80W/cm² high pressure Hg lamp at 10m/min of conveyor speed.

and glass was good until 10 wt% of OXA. With higher content of OXA, the flexibility of the coating was improved. The surface cure rate, measured on a conveyor type UV irradiator, was decreased by adding 20 wt.% of OXA. On the other hand, the exo-therm curve became sharper and bigger by adding larger amount of OXA, showing the higher rate of ring opening reaction in the formulation (Figure 4).

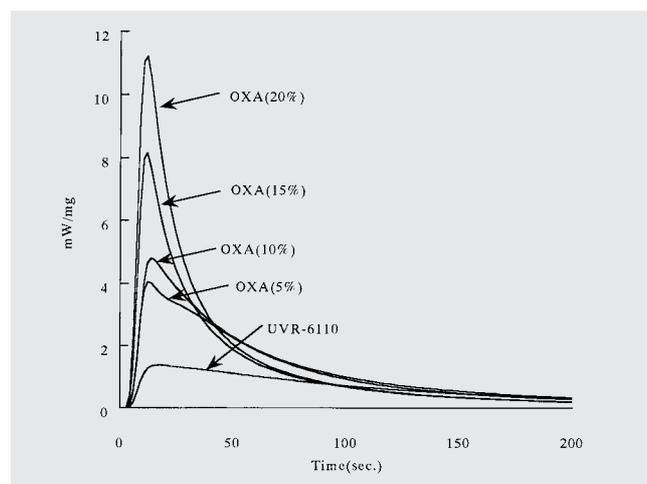


Figure 4. Photo-DSC exo-therm curves for OXA and UVR-6110 formulations ($I=20.0\text{mW/cm}^2$ at 365nm, 3parts of UVI-6990, 40)

In cationic ring opening polymerization, hydroxy-functional materials such as alcohol is known to work as a chain transfer agent. OXA possesses not only oxetane ring, which undergoes cationic polymerization, but also hydroxy methyl group. With lower concentration of OXA in the formulation, the hydroxy group should work as chain transfer site and accelerate cure rate. The higher content of hydroxy group in the formulation should lead to shorter polymer chain length, which results in a weaker surface of the coating, and might decrease the cure rate. Another possibility for lower rate is the existence of remaining un-reacted hydroxy

group in the coating, which should increase the tackiness of the surface.

The Photo-DSC curves for the 30 wt% of oxetanes (EHOX, POX, DOX and XDO) formulations were shown in Figure 5. The heat generation curves for all the oxetane formulations were narrower compared with that for UVR-6110 alone, exhibiting high reactivity of the formulations.

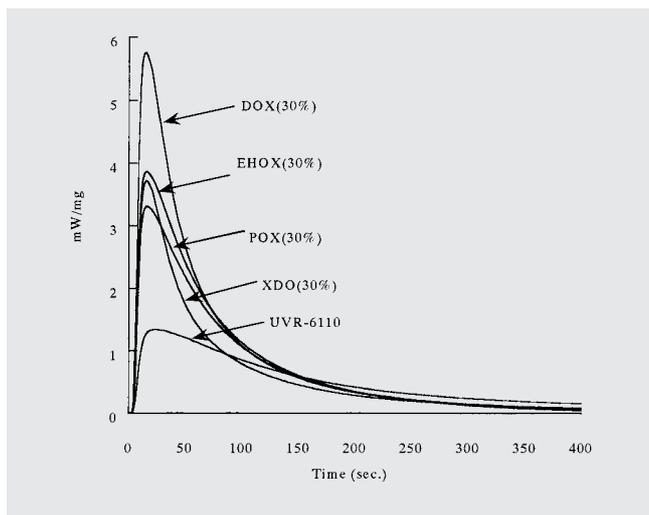


Figure 5. Photo-DSC exo-therm curves for POX, EHOX, DOX and XDO with UVR-6110 formulations (I=20.0mW/cm² at 365nm, 3parts of UVI-6990, 40)

The formulations of EHOX and POX are shown in Table 3. EHOX with long alkyl side chains gave low viscosity formulations. Although the oxetane monomers are mono-functional, surface cure rates were higher than that of epoxide alone. The adhesion of the formulations for PC and glass was poor compared with the UVR-6110 alone. The flexibility of the coatings were improved by the formulation of either EHOX and POX.

Table 3 Formulations of EHOX, POX and OXA with UVR-6110¹⁾

UVR-6110 ¹⁾	100	70	70	80	60	80	60
EHOX		30		10	30		
POX			30			10	30
OXA				10	10	10	10
UVI-6990 ¹⁾	3	3	3	3	3	3	3
Viscosity(cps) ²⁾	375	53	116	103	39	142	76
S.C.R.(mpm) ³⁾	20	>50	>50	>50	>50	>50	>50
Adhesion ⁴⁾	PC	OK	NG	NG	NG	NG	NG
	Steel	OK	OK	OK	OK	OK	OK
	PMMA	NG	NG	NG	NG	NG	NG
	Glass	OK	NG	NG	NG	NG	NG
Flexibility ⁴⁾	8mm	NG	OK	OK	OK	OK	OK
	6mm	NG	OK	OK	OK	OK	OK
	4mm	NG	OK	OK	OK	OK	NG
	2mm	NG	OK	NG	NG	OK	NG

1) Union Carbide
 2) Measured at 25°C
 3) S.C.R.; Surface Cure Rate. Coatings applied to steel panel with a #3 bar and cured with 80W/cm² high pressure Hg lamp at varied conveyor speed (mpm; meter per minute)
 4) Measured according to JIS K-5400, Coatings applied with a #3 bar and cured with 80W/cm² high pressure Hg lamp at 10m/min of conveyor speed.

The formulations of di-functional oxetanes (XDO and DOX) were listed in Table 4. While the formulation with XDO exhibited rather small decrease in viscosity, DOX reduced viscosity effectively. In the combination of XDO with OXA, the viscosity of the formulation was also low. Each formulation showed very high surface cure rate. In the formulation of OXA and XDO, even with 20 wt.% of OXA, the cure rate over 50 m/min was achieved. Same as the mono-functional oxetanes, the adhesion of the formulations were poor. This low adhesion might be explained by stress concentration between the surface of substrate and the cured coating caused by fast polymerization of oxetane ring. Combination with OXA, slightly improved the flexibility of the coatings.

Table 4 Formulations of XDO, DOX and OXA with UVR-6110¹⁾

UVR-6110 ¹⁾	100	70	70	80	70	50	50
XDO		30		10	20	30	
DOX			30				30
OXA				10	10	20	20
UVI-6990 ¹⁾	3	3	3	3	3	3	3
Viscosity(cps) ²⁾	375	277	102	184	176	105	48
S.C.R.(mpm) ³⁾	20	>50	>50	>50	>50	>50	>50
Adhesion ⁴⁾	PC	OK	NG	NG	NG	NG	NG
	Steel	OK	OK	OK	OK	OK	OK
	PMMA	NG	NG	NG	NG	NG	NG
	Glass	OK	NG	NG	NG	NG	NG
Flexibility ⁴⁾	8mm	NG	OK	NG	OK	OK	OK
	6mm	NG	NG	NG	OK	OK	NG
	4mm	NG	NG	NG	NG	NG	NG
	2mm	NG	NG	NG	NG	NG	NG

1) Union Carbide
 2) Measured at 25°C
 3) S.C.R.; Surface Cure Rate. Coatings applied to steel panel with a #3 bar and cured with 80W/cm² high pressure Hg lamp at varied conveyor speed (mpm; meter per minute)
 4) Measured according to JIS K-5400, Coatings applied with a #3 bar and cured with 80W/cm² high pressure Hg lamp at 10m/min of conveyor speed

For the cationic curing system using epoxy monomers, it is well known that post cure is required for complete cure of the coating. Coating of UVR-6110 alone exhibited very poor acetone resistance until 24 hours after the irradiation. As shown in figure 6, addition of oxetane monomers improved the acetone resistance even 10 minutes. Higher amount of oxetane content increased the acetone resistance. The improvement effect could be explained by the fast generation of the cross-linked network of oxetanes accelerated by epoxide. The

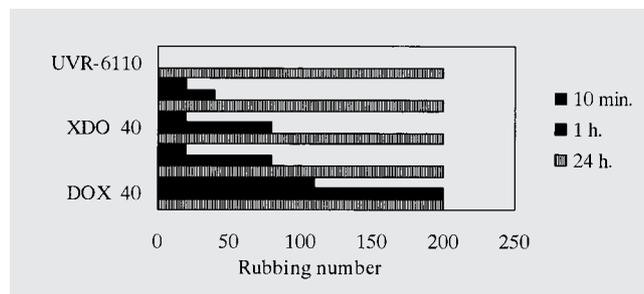


Figure 6. Acetone Resistance vs. Time

References

higher acetone resistance of DOX formulation can be explained by lower molecular weight per oxetane group of DOX, which resulted in shorter length of cross-links i.e. a stronger network.

4 Conclusion

Oxetanes are reactive monomers effective for photo-cationic curing systems. All the monomers were completely miscible with UVR-6110 and were AMES Test negative.

Formulating with cyclo-aliphatic diepoxide, accelerated the polymerization rate of oxetanes. MPO, possessing electron donating p-methoxyphenyl group in the 2nd position of oxetane ring, was proved to work as a good accelerator for other oxetane monomers without such group.

In the formulation with monofunctional oxetanes with epoxide, the viscosity of the formulations was reduced effectively. HOX with long alkyl side chains exhibited the lowest viscosity while keeping the surface cure rate high.

In the difunctional oxetanes formulation, DOX alone and the combination of XDO with OXA gave low viscosity formulations with high surface cure rate. Addition of difunctional oxetane monomers improved acetone resistance. Higher amount of oxetane content increased acetone resistance.

As investigated in this study, mono- or di-functional oxetane monomers provide cationic UV-curing formulations of epoxide with high cure rates and low viscosity. This viscosity reduction could be advantageous for some applications such as coating industry.

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本報告は、Radtech North America 2000にて発表を行った予稿集に加筆、修正したものである。

オキセタン化合物：光カチオン重合における硬化特製

オキセタンプロジェクト 佐々木 裕

四員環の環状エーテルであるオキセタンは光カチオン重合においてエポキシドとは異なる重合特性を示す事が明らかになっている。本報告においては、重合性官能基としてオキセタニル基を有するモノマーを用いて、フォト-DSCを用いた光カチオン重合挙動の評価および市販の脂環式エポキシであるUVR-6110(ユニオン・カーバイド社製)との配合物の特性評価を行い、オキセタン系材料の光硬化型材料への応用を検討した。フォト-DSCによる重合時の発熱量の測定から、オキセタン環の2位にp-メトキシフェニル基を導入したMPOは単独重合のみならず、無置換のオキセタンモノマーであるPOXとの共重合においても重合を促進する事が明らかになった。

工業化が予定されている5種類のモノマーは、一般的な脂環式エポキシであるUVR-6110(ユニオン・カーバイド社製)との相溶性は良好であり、比較的分子量が低いにもかかわらず Ames 試験が陰性であった。また、側鎖に2-エチルヘキシル基を有するEHOXは希釈性および表面張力低下能に優れていた。UVR-6110との配合により光硬化型材料への応用の検討を行い、単官能オキセタン化合物の添加により配合物の粘度を大きく低減する事ができる事、二官能オキセタン化合物の配合により脂環式エポキシモノマー単独の場合と比較して照射後の耐溶剤性が大きく向上できる事が明らかになった。