

# Multifunctional isocyanate monomer for UV curable applications

Yotaro Hattori, Showa Denko K.K., Tokyo, Japan  
Shao Songhai, Showa Denko K.K., Tokyo, Japan  
Siyi Qu, Showa Denko America Inc., New York, United states

## Abstract

Multifunctional isocyanate monomers, which contain isocyanate and double bond moieties, have been designed for performance enhancement of radiation curing formulations. It is found that the isocyanate groups in this series of monomers possess high reactivity compared to conventional isocyanates, thus they can be used to moderate reaction conditions or reduce the catalyst amount. The result shows that its unique structure also contributes to high UV sensitivity. Here, we report these properties and application data for the UV curing system.

## Introduction

Isocyanate group including multifunctional vinyl monomers (hereinafter referred to as “isocyanate monomer”) are useful raw materials of crosslinker, acrylic poly-isocyanate, urethane oligomer or polymer. Examples of isocyanate monomers include: (meth)acryloyloxyethyl isocyanate (IEM)<sup>1,2,3</sup>, methacryloyloxy isocyanate(MAI)<sup>4,5</sup>, 3-isopropenyl- $\alpha,\alpha$ -dimethylbenzyl isocyanate(TMI)<sup>6,7</sup> and so on. Isocyanate monomers can be homopolymerized or copolymerized with a number of other vinyl monomers to provide a poly-isocyanate. On the other hand, isocyanate group can react with active hydrogen-containing materials to insert double bonds. Synthesized vinyl substance can propagate with other vinyl monomers through chemically or radically initiated free radical reactions as well.

## Aliphatic isocyanate monomer

At first, (Meth) acryloyloxyethyl isocyanate was developed as a multifunctional monomer including aliphatic isocyanate and polymerizable (meth)acrylate group. Each group can be reacted independently without affecting the other. The formulation of IEM was first revealed by Rohm and Haas in 1955<sup>1</sup>, where the isocyanate esters of acrylic and crotonic acids were described simultaneously. Since the report of this

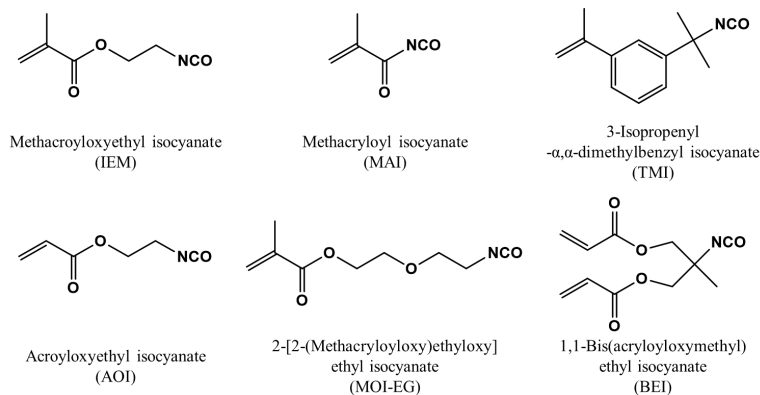


Fig. 1 Chemical structure of isocyanate monomer.

patent, many related studies had also been reported by various researchers<sup>8,9</sup>. The first commercial production of methacryloyloxyethyl isocyanate was developed by Dow Chemical via oxazoline chemistry using derivative of commercially available ethyl oxazoline<sup>3</sup>. With the increasing availability, more information has appeared in the literature, notably on coatings applications. Following this, the other aliphatic isocyanate monomers have developed<sup>10,11</sup>. Furthermore, application patent of dental<sup>12</sup>, contact lens<sup>13</sup>, UV repeat adhesive<sup>14</sup>, fluorine polymer<sup>15</sup>, color filter resin<sup>16</sup>, resist resin for printing plate<sup>17</sup>, adhesives<sup>18</sup>, resist resin for semiconductor<sup>19</sup>, Solder mask<sup>20</sup> etc. are reported. On the other hand, many types of aliphatic isocyanate monomer were developed, including MAI<sup>4,5</sup>, AOI<sup>2</sup>, BEI<sup>21</sup>, MOI-EG<sup>22</sup> (**Fig. 1**).

## Chemical property

Reactivity of NCO group is greatly influenced by the electron-withdrawing property and steric hindrance of the adjacent substituents. Some examples of NCO group's reactivity data are showed as follows.

As for the reaction conditions, *n*-butanol was used 3 times more in molar ratio to that of the isocyanate monomer, in toluene solvent, at 60°C, without catalyst conditions. Conversion of NCO was analyzed by quantitatively measuring 2250cm<sup>-1</sup> peak of NCO group in FT-RI. Generally, it is known that aromatic isocyanates show greater reactivity compared to aliphatic type. Here, the error due to reactivity differences of two NCO groups in di-isocyanate is ignored. As can be seen from the **Fig. 2**, MOI and AOI tend be more active compared to the same type of primary aliphatic di-isocyanate "HDI". The high reactivity of MOI be resulted from the electronic factors or intramolecular interactions. The sequence of reactivities for IPDI, hydrogenated MDI, and TMI is thought to be affected by steric hindrance of NCO groups. MAI shows extremely high reactivity due to the effect of electron withdrawing property of the carbonyl group. This has been reported in some literatures already<sup>4</sup>.

With respect to copolymerizability, TMI is reported to be equivalent to  $\alpha$ -methylstyrene. MOI, AOI and MOI-EG can be also used in the same way as general (meth) acrylates. As an example, **Table 1** shows the Q and e values of MOI, MAI, and TMI.

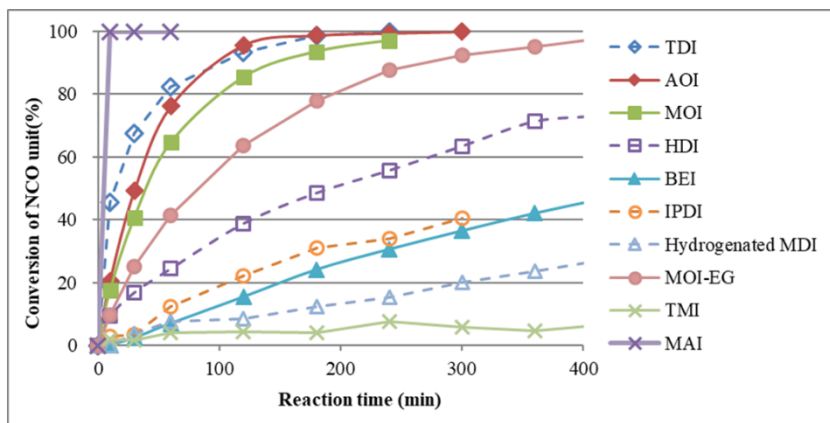


Fig. 2 Reactivity comparison of isocyanate groups

	MOI	MAI	TMI
r1*1	0.49*2	0.35*3	0.72*4
r2*1	0.54*2	0.77*3	0.80*4
Q	0.74	0.52	2.26
e	0.35	0.34	-1.54

Table. 1 Parameter of Q and e score

## Urethane (meth) acrylate derivatives of isocyanate monomer

As it's mentioned in introduction, isocyanate monomer possess two functional groups and therefore can be modified two ways depending on which functional group is reacted first. In here, we will discuss about properties of urethane acrylate which is prepared by reacting isocyanate part first. Urethane acrylate is known for toughness, low percentage of curing shrinkage and high chemical resistance. It is widely used as a radical curable resin for industrial materials, electronic materials and so on. In general, the radical reactivity of urethane (meth) acrylate is better than that of ester acrylate. This is because oxygen diffusion is inhibited due to the high cohesive force of urethane bonds that is causing higher viscosity of urethan acrylate<sup>23,24</sup>.

**Fig. 3** shows the conversion of unsaturated groups, when various curable monomers were mixed with a photoinitiator and irradiated with ultraviolet light, using a high-pressure mercury lamp as a light source under ambient condition. The conversion is quantified by using the FT-IR with a wavenumber at  $810\text{cm}^{-1}$ . As shown in the figure, in general, the conversion of ester acrylate follows acryl> methacryl. On the other hand, the urethane methacrylate prepared by using MOI has a similar reactivity compared to ester acrylate, despite the reactive group is a methacrylic. It shows the photosensitivity of urethane methacrylate using MOI is higher than using ester methacrylate.

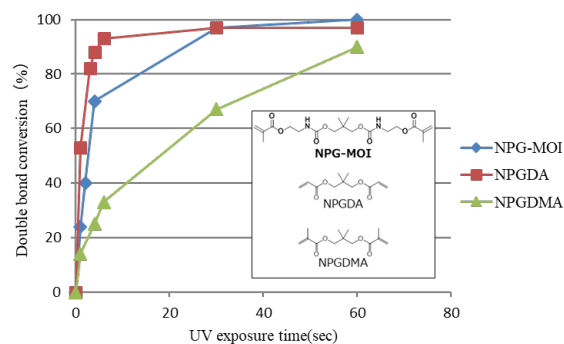


Fig. 3 Comparison of reactivity under UV exposure.

### Acrylic resin including unsaturated group prepared by using isocyanate monomer

Since isocyanate group has high reactivity to various activated hydrogen groups, it can even easily insert double bond to high molecular weight acrylic polyol. In here, we introduce UV repealing adhesives as the example and show the related features.

Since a polymer adhesive is required to have high peeling force and cohesive force, the polyacrylic adhesive is typically prepared with a high molecular weight (Mw, several hundreds or thousands  $\text{kg mol}^{-1}$ , calculated by using the polystyrene reference). In turn, it is tough to insert double bond to this class of polymers, since they are highly viscous due to their own entanglement. In addition, steric hindrance of the polymers may make it difficult to further react with activated hydrogen group of the acrylic polymer. At first, we show the results of an attempt to synthesize polymer B as UV re-peeling adhesive by inserting double bond using AOI.

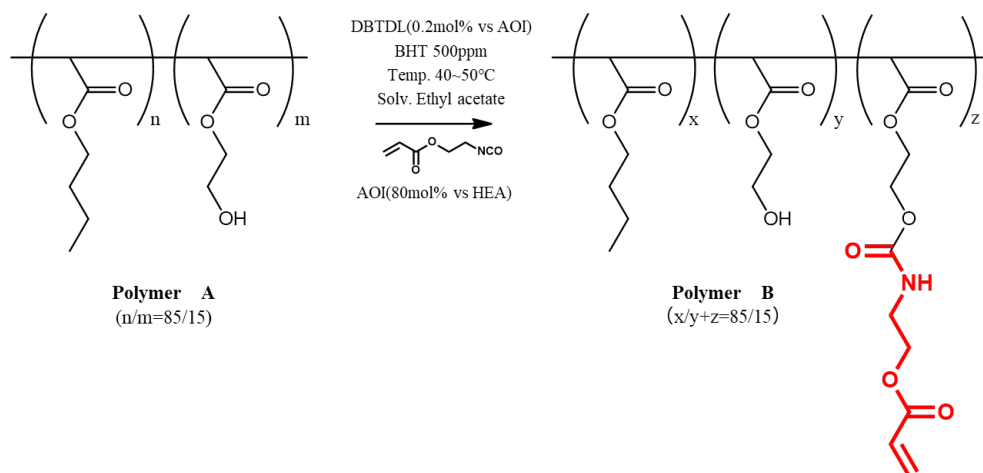


Figure 4 synthesis of AOI adducted acryl polymer for UV re-peeling adhesive.

The finishing point of the urethanation was determined by tracking the remaining isocyanate group monitored by using the FT-IR. As a result, the peak of the NCO group was disappeared in 2 hours. Reaction scheme is shown in **Fig. 4**. Then, we confirmed irradiating UV light to the obtained polymer B decreased its peeling force. We performed the thin-film characterization using the following protocol: a composition containing the polymer B and crosslinker are coated on a  $50\mu\text{m}$  PET film with a dry film thickness of  $30\mu\text{m}$ . Then, the peeling force after curing at  $40^\circ\text{C}$  for 3 days was initially measured, and was compared to the peeling force value after irradiating a predetermined amount of UV light. As a result,

the peeling force was reduced after UV irradiation. It is considered that such changes in properties are due to the dramatic changes in mechanical properties, surface tension, and compatibility of the adhesive due to UV irradiation<sup>25</sup>.

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