Highly Sensitive α-Acyloxy methacrylate Cross-linking Agents with High Curability in the Presence of Atmospheric Oxygen

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A highly sensitive photopolymerization system under atmospheric conditions are desired in industry, such as the field of printing plates widely used in commercial printing. We have developed a new series of α-acyloxy methacrylate cross-linking agents which exhibit an excellent curability even in the presence of atmospheric oxygen. Molecular orbital calculations indicate that the formation enthalpy of inhibition reaction by oxygen is much less favorable than that of polymerization for α-acyloxy methacrylate compared to conventional acrylates or methacrylates. The new cross-linking agents realized photopolymerizable printing plates without any oxygen barrier layer.

Keywords: photopolymerization system, α-acyloxy methacrylate, visible laser

1. Introduction

Photopolymerizable compositions are useful material technologies which have been used in various industrial fields including adhesives, color resist inks, ink jet-printing inks, printing plates, and three-dimensional molding. As a critical issue in technologies of photopolymerizable compositions, improvements in sensitivities (improvements in polymerization-initiating efficiencies, polymerization speed and polymerization reaction rates) can be mentioned.

For example, as for adhesives, inks, etc., it is required to improve the sensitivities in order to improve the curing rates and the strength of cured films. In addition, in printing plates compatible with visible lasers [1], etc., it is required to improve the sensitivities for higher productivity or efficient energy saving.

With regard to such photopolymerizable compositions, cationic polymerizations such as for epoxies or radical polymerizations such as for acrylates have widely been used [2].

With regard to features of cationic polymerizations, it is possible to conduct the polymerization reaction under the presence of the air. However, the polymerization reactivity is insufficient, and therefore, if higher reactivity is required at room temperature, there is a limitation in which this forces selection of materials exhibiting inferior storage stability.

On the other hand, with regard to features of radical polymerizations, the polymerization reaction speed is higher with generation of heat, and materials exhibiting superior storage stability can be selected. However, on the contrary, polymerization inhibition by oxygen (radicals are captured by oxygen molecules in the air, thereby terminating polymerizations) possibly occurs, and therefore, conditions for use are somewhat limited (e.g. requirements of exposure under vacuum or provision of a layer insulating the photosensitive layer from oxygen).

Photopolymerizable compositions for radical polymerizations are comprised of initiators (or initiator systems which include sensitizing dyes besides initiators) which generate radicals through light exposure, and polymerizable compounds (or polymerization systems which also include alkali-soluble polymers) which are cured through the polymerization by the initiation radicals. As attempts to reduce polymerization inhibition by oxygen, an approach based on initiators [3] and an approach based on polymerizable compounds [4] have been reported.

In particular, the approach based on polymerizable compounds which has a significant influence on the polymerization speed and the
reaction rate is important. However, any polymerizable compounds that combine high sensitivity and superior storage stability have not yet been discovered.

We have discovered new α-acyloxy methacrylate polymerizable cross-linkers which are capable of reducing polymerization inhibition by oxygen. In this article, we report studies on the new cross-linkers.

2. Experimental
2.1. Analysis Equipment
A 1H NMR spectrometer (“Gemini 300” manufactured by Varian Inc.) was used for structural identification. An HPLC system (“Waters 600” manufactured by Waters Corporation) was used for isolation/purification and purity analysis. A gas chromatography (GC) system (“GC-9A” manufactured by Shimadzu Corporation) and a GPC system (manufactured by Tosoh Corporation) were used for analysis on speed of monomer reactions. A molecular modeling software “CaChe” (supplied by FUJITSU) based on the MOPAC PM3 UHF method was used for molecular orbital (MO) calculations.

2.2 Synthesis of α-acyloxy methacrylates (Me2X, Me4X, X2-X8, Y1 and Y2)
α-acyloxy methacrylates (Me2X, Me4X, X2-X8, Y1 and Y2) were synthesized according to Scheme 1. Their colors, shapes, and melting points are shown below with their molecular structures (Fig. 1).

Scheme 1. Synthesis of α-acyloxy methacrylates
Me2X: colorless oil
Me4X: colorless oil
X2: white solid, m.p. 106.0-107.0 °C
X3: white solid, m.p. 70.5-71.0 °C
X4: white solid, m.p. 74.4-75.5 °C
X5: white solid, m.p. 66.2-67.0 °C
X6: white solid, m.p. 70.6-72.0 °C
X7: white solid, m.p. 67.6-68.9 °C
X8: white solid, m.p. 72.9-74.0 °C
Y1: white solid, m.p. 61.1-62.0 °C
Y2: white solid, m.p. 37.3-38.0 °C

2.3 Evaluation on polymerizabilities in a solution system
A 1-methoxy-2-propanol solution containing a polymerizable compound (0.39 mol/L) to be evaluated, an azo-based thermal polymerization initiator (“V-65” manufactured by Wako Pure Chemical Industries, Ltd., 0.01 mol/L), and an internal standard material of hexyl acetate (0.39 mol/L) was prepared, and, the solution was heated to 65°C. At intervals of 15 minutes, a portion of the reaction solution was harvested, and molecular weights of produced polymers were measured by using the GPC while the amount of monomers consumed in the reaction was measured by the GC (SE30 column was used). The results of the GC measurement were analyzed by the pseudo-first-order plot to calculate the polymerization reaction speed.

2.4 Preparation of evaluation plate materials
1) For UV exposure: a model plate material was prepared by providing on a hydrophilized aluminum support a photopolymerizable photosensitive layer which was comprised of a titanocene initiator (Fig. 2), a polymerizable cross-linker to be evaluated, an alkali-soluble polymer (a copolymer of allyl methacrylate/methacrylic acid (80/20), the weight average molecular weight: 43,000) and a pigment.
2) For laser exposure: a plate material was prepared by combining an aminocoumarine sensitizing dye (Fig. 2) to correspond to a laser light source in the above-described model plate material (Fig. 3).

Fig. 1 Molecular structures of α-acyloxy methacrylates
Fig. 2 Molecular structures of an initiator and sensitizing dyes
2.5 Evaluation on polymerizabilities (insolubilization ratio) in a coating system

Plate materials prepared in Section 2.4 were surface-exposed to light in Eye Rotary Printer (“RP311” manufactured by EYE GRAPHICS CO., LTD.; a mercury lamp was used) where the exposure conditions were adjusted so that the light of a wavelength of 405 nm generated an intensity of 5.0 mJ/cm² at the printing surface. After exposure, the plate materials were heated at 120°C for 20 seconds. Then, the plate materials were immersed in a mixture of 2-methoxypropanol/acetone (1:1) for two hours, and then, were dried.

The weight change before and after the exposure was expressed in percentage, and was regarded as an insolubilization ratio (when the photosensitive layer completely remains by exposure curing, a value of 100% is obtained).

In addition, in order to eliminate influences of differences in the length of time from completion of the exposure to measurement of the weight changes on the polymerization reaction (in order to even out fluctuations concerning measurement accuracy), the plate materials were heated directly after the exposure.

Furthermore, in order to estimate degrees of polymerization inhibitions due to differences in the oxygen concentrations, polymerizability was evaluated while varying a degree of vacuum.

2.6 Evaluation on Laser sensitivities

The plate materials for laser exposure prepared in Section 2.4 were exposed to a laser beam under the conditions of 4000 dpi, 175 lpi, and 1.50 mJ/cm² with Platejet4 (manufactured by CSI), which is an exposure machine equipped with an FD-YAG laser (wavelength: 532 nm), and then, were subjected to photographic processing with an automatic processor “LP-850P II” (manufactured by Fuji Film Corporation; a developing solution “LP-D” was used), thereby forming images (Fig. 4). With respect to the resulting printing plates, image-forming sensitivities were evaluated.

Additionally, the above-described evaluation plate materials were allowed to stand at room temperature for 3 days, and the sensitivities were calculated in the same manner. Plate materials which exhibited no changes in the sensitivities before and after allowing them to stand at room temperature correspond to plate materials having superior storage stability.

3. Results and Discussion

3.1 Guidance for molecular design

Widely-used polymerizable compounds such as acrylates and methacrylates are susceptible to polymerization inhibition by oxygen. This aspect will be discussed below, focusing on each reaction process of radical polymerizations.
Among reaction processes of radical polymerizations, there are mainly i) an initiation process in which initiation radicals react with polymerizable compounds to generate radical growing ends; and ii) a propagation process in which, with respect to the radical growing ends, polymerizable compounds continuously undergo a chain polymerization reaction to form a polymer.

On the other hand, as to processes of inhibiting the polymerization propagation, there are iii) an O₂-termination process (polymerization inhibition by oxygen) in which oxygen reacts with the radical ends to terminate the polymerization; and iv) a (recoupling) termination process in which radical growing ends react with one another to thereby terminate the polymerization.

Consequently, the three reaction processes of the propagation, O₂-termination and recoupling termination always compete with one another, and the polymerization inhibition by oxygen will occur when the reaction speed of oxygen with the radical growing ends is higher than the reaction speed of polymerizable compounds (Fig. 5).

![Fig. 5 Calculation model for each polymerization reaction process](image)

### Table 1. Formation enthalpy of each reaction process

| Z       | ΔHi  | ΔHp  | ΔHo₂ | ΔHrc |
|---------|------|------|------|------|
| CH₂OCOMe | -21.6 | -12.5 | -0.8  | -16.6 |
| CH₂OCOPh | -21.8 | -12.5 | -0.8  | -20.3 |
| CH₂OH    | -13.8 | -24.6 | -11.1 | -34.5 |
| CH₂OMe   | -13.0 | -19.5 | -9.6  | -36.1 |
| H        | -21.1 | -20.9 | -8.2  | -39.8 |
| Me       | -19.6 | -16.0 | -3.4  | -20.5 |
| Bu       | -19.0 | -0.9  | +2.6  | +28.5 |
| CH₂CO₂Me | -21.4 | -5.3  | +1.0  | -13.7 |

*Z = a

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Table 2. Polymerizabilities of α-acyloxymethacrylates

|       | BuA          | BuMA         | Me2X         | Me4X         |
|-------|--------------|--------------|--------------|--------------|
| Rp (mol/L/s) a | 4.9×10^{-5}  | 3.5×10^{-5}  | 3.7×10^{-5}  | 3.2×10^{-5}  |
| Mn b           | 3.6×10^3     | 7.1×10^3     | 4.3×10^3     | 4.1×10^3     |

a Polymerization speeds were determined by GC analysis.

b Number average molecular weights were determined by GPC analysis.

Therefore, in order to search for novel polymerizable compounds (or polymerizable groups) that exhibit low reactivities with oxygen, a likelihood of each reaction process (formation enthalpy $\Delta H$) was estimated by the MO calculations with compounds having structures similar to acrylates (Table 1).

As seen in Table 1, it is evident that, although acrylates ($Z=H$) or methacrylates ($Z=Me$) are likely to undergo polymerization propagation ($\Delta H_p$ is negatively larger), they are likely to undergo the recoupling termination ($\Delta H_{rc}$ is negatively larger), and also, are susceptible to polymerization inhibition by oxygen ($\Delta H_{o2}$ is negative).

In addition, it has been known that itaconates ($Z=CH_2CO_2Me$) having little polymerizabilities, and that tert-butyl acrylate ($Z=\text{tBu}$) [5] does not polymerize. Therefore, it is confirmed that the calculation results are reasonable.

On the other hand, α-acloyxymethacrylates ($Z=CH_2OCOMe$) [6], for which it has been reported that the compound has almost the same likelihood of polymerization propagation as that of methacrylates and that recoupling termination is unlikely to occur, also support validness of the calculation results. Then, calculated results of α-acloyxymethacrylates lead to a new understanding that polymerization inhibition by oxygen is unlikely to occur in α-acloyxymethacrylates.

We have deduced that this outcome was attributed to an electronic factor and a steric factor caused from substitution with an acyloxy group at the $\alpha$ position.

That is, addition of the radical growing ends to polymerizable compounds dominantly proceeds by electron-withdrawing effects of acyloxy groups, and this leads to almost the same likelihood of polymerization propagation as that of methacrylates.

Furthermore, due to the steric hindrance of acyloxy groups, termination of the polymerization by binding of radical growing ends is unlikely to occur. Rare occurrence of the termination reaction further allows the polymerization growth reaction to dominantly proceed.

Meanwhile, acyloxy groups act on added oxygen molecules, exhibiting effects of steric hindrance or electronic repulsion against them, and thus, unstabilize adducts of radical growing ends and oxygen molecules. Such an action would be considered as a factor which makes it more difficult for the reaction of the radical growing ends with oxygen to occur, than acrylates or methacrylates do.

3.2 Polymerizabilities of α-acyloxy methacrylates (solution system)

In order to confirm the above-described calculation results in experiments, two types of α-acyloxy methacrylates were synthesized, and their polymerization speeds $R_p$ and number average molecular weights $M_n$ of produced polymers were determined (Table 2).

As seen in Table 2, it is evident that α-acyloxy methacrylates (Me2X and Me4X) have almost the same polymerizabilities (polymerization speeds $R_p$ and number average molecular weights $M_n$ of produced polymers) as that of acrylate (BuA) or methacrylate (BuMA).

3.3 polymerizabilities of α-acyloxy methacrylates (coating system)

Next, in order to estimate degrees of polymerization inhibition by oxygen, the polymerizabilities were evaluated in a coating system in which the radical mobility is low.

The design of α-acloyxymethacrylates was changed to a structure of a polymerizable cross-linker having a number of polymerizable groups within one molecule (a polyfunctional form) in order to measure an insolubilization behavior of the cured film.

Specifically, bifunctional forms (compounds X2 and X3 having two polymerizable groups) as well
as trifunctional forms (compounds Y1 and Y2 having three polymerizable groups) were synthesized, and their polymerizabilities were evaluated by comparing them with a tetrafunctional form of an acrylate (PETA) which has been widely used (Fig. 6).

As seen in Fig. 6, it is evident that, although polymerization degrees of all polymerizable cross-linkers decrease as the quantity of oxygen is increased from the high vacuum state to the atmospheric pressure state, bifunctional form X3 is insolubilized even under the atmospheric pressure, and is tolerant to polymerization inhibition by oxygen. On the other hand, such effects could not be observed in bifunctional form X2 as well as trifunctional forms Y1 and Y2.

It is considered that, in X2 having a shorter length of a linking chain between polymerizable groups or the trifunctional forms having lower molecular mobility, their polymerization growth is slower, and therefore, they are susceptible to influences of oxygen.

Therefore, the length of the linking chains between polymerizable groups in the bifunctional forms was changed, and influences brought by the changes were evaluated (Fig. 7).

![Fig. 6 Polymerizabilities of α-acyloxy methacrylate cross-linkers](image)

![Fig. 7 Influences of the length of linking chains in bifunctional cross-linkers](image)
As seen in Fig. 7, it is evident that the polymerizabilities under the presence of oxygen increase when the linking chain number is 7 (n=7; X7) or less, while the polymerizabilities decrease when the linking chain number is 8 (n=8; X8) or higher.

It is interpreted as follows: since, at a linking chain number of 2-4 (n=2-4; X2-X4) where the linking chains are short, the distance between polymerizable groups within the molecule is too close, the reaction with polymerizable groups in adjacent molecule is inhibited by steric hindrance caused by such a close distance between polymerizable groups, and the reaction of the groups with oxygen molecules, the size of which is smaller, predominantly proceeds. Furthermore, it is deduced as follows: when the linking chain number is 8 (n=8; X8) where the linking chains are long, since the proportion of polymerizable groups occupying one molecule is smaller, the density of polymerizable groups present in the coating film is reduced, and the reaction of the polymerizable groups with oxygen molecules more predominantly proceeds than the polymerization does.

3.4 Polymerizability of a mixture of cross-linkers (coating system)

Next, a mixture (mixing weight ratio of 1:1) of α-acyloxy methacrylate cross-linkers was evaluated. Evaluation results are shown in Fig. 8.

As seen in Fig. 8, it is evident that α-acyloxy methacrylate (X7) can reduce polymerization inhibition by oxygen even in the 1:1 mixture system of X7 and an acrylate (PETA).

We have generated two hypotheses to explain the results.

Hypothesis (I): if, based on differences in reactivities of polymerizable groups, it is deduced that the reaction proceeding from radicals of growing ends of the α-acyloxy methacrylate, which is insusceptible to influences of oxygen, to the acrylate is slower, while the reaction proceeding from radicals of growing ends of the acrylate to the α-acyloxy methacrylate is faster, then, this means that the reactivities of radicals of growing ends of the α-acyloxy methacrylate, which is insusceptible to influences of oxygen, are dominant, leading to the above-described results.

Hypothesis (II): a state where the radical mobility is reduced due to polymerization curing is more susceptible to influences of oxygen. From this point of view, polymerization of highly-polymerizable acrylates completes before the film is hardened, and remaining α-acyloxy methacrylates undergo polymerization even after the film is hardened, while suppressing their reactivities with oxygen, thus leading to the above-described results.

In order to explore in more details the competition between the reaction with oxygen and the polymerization propagation reaction with respect to each polymerizable cross-linker, differences in the insolubilization rate depending on the time of allowing plate materials to stand after the exposure were studied where the heating treatment after exposure was omitted (Fig. 9).
As seen in Fig. 9, it is evident that, while, in the mixture system of only \( \alpha \)-acyloxymethacrylates (Y2/X7), sufficient insolubilization rates are obtained from the early stage even without the heating treatment, the progress of polymerization (insolubilization rate) in the mixture system of the \( \alpha \)-acyloxymethacrylate and the acrylate (X7/PETA) is slower, and the mixture system is very susceptible to influences of oxygen in a case where the heating treatment is omitted. That is, it is understood that, in the mixture system of \( \alpha \)-acyloxymethacrylate and the acrylate, the heating treatment is required in order to make the polymerization proceed.

These results support both of the above-described hypotheses, and it is considered that phenomena of both the hypotheses occur in actual systems.

3.5 Actual evaluation based on a laser exposure system

With respect to plate materials in which the new mixture system of \( \alpha \)-acyloxymethacrylate cross-linkers (Y2/X7) found in Section 3.4, the image-forming sensitivity was actually evaluated based on exposure to a 532 nm FD-YAG laser beam. As a result, the sensitivity was 0.22 mJ/cm\(^2\) (any image cannot be formed with conventional PETA), and the storage stability was also superior.

Thus, it is understood that, even when \( \alpha \)-acyloxy-methacrylate cross-linkers are used in plate materials for laser exposure, they reduce polymerization inhibition by oxygen, and substantially achieve high sensitivities.

4. Conclusion

We discovered new \( \alpha \)-acyloxymethacrylate cross-linkers which reduce polymerization inhibition caused by oxygen. It is deduced that this feature is attributed to dominancy of the polymerization propagation reaction over the polymerization termination due to the presence of oxygen or the recoupling termination in terms of formation enthalpies.

Furthermore, we successfully realized plate materials without an oxygen-insulating layer, which had been difficult to produce with conventional acrylate cross-linkers, by use of these polymerizable cross-linkers. It is expected that these polymerizable cross-linkers will be applied to various industrial fields using photopolymerizable compositions also in the future.

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