Cyclopolymerizable UV Monomers Introducing Tetrahydrofuran Rings into the Polymer Backbone.

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1. INTRODUCTION

Polymers with cyclic structures on the backbone (cyclopolymers) are widely used to improve heat resistance, mechanical strength, and transparency of products. Synthesis methods of those cyclopolymers can be classified into following three types depending on when the ring structure is formed: (a) Polymerization of cyclic monomers (the cyclic structure originally exists in monomers), (b) post-cyclization reaction of polymers, and (c) simultaneous formation of cyclic structures during polymerization (cyclopolymerization). Most industrial cyclopolymers are manufactured by technique (a) or (b). Although numerous references have appeared for the past decades[1], there are limited number of practical examples on cyclopolymerization because of difficulty linking structural features to product superiority. A few prominent practical examples are cyclopolymerization of diallyl quaternary ammonium salts (the first example of cyclopolymerization[2,3]) and of perfluoro-1,6-diene[4] (Figure 1).
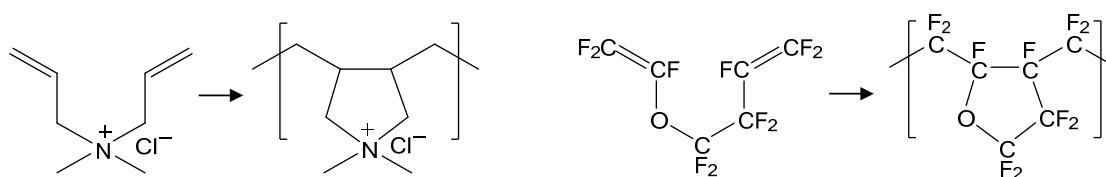

Figure 1. Examples of cyclopolymerization in commercial use

Recently, we found that well-known cyclopolymerizable monomer, Methyl 2-(allyloxymethyl) acrylate (AOMA[TM]) has enough reactivity and excellent properties to use for UV curing applications. After those findings, we developed an industrial production method of AOMA and further examined the synthesizability and functional characteristics of AOMA derivatives (various esters, acid, and salts). In this paper, we describe the general knowledge of cyclopolymerization and report the typical characteristics of "AOMA[TM] series" (AOMA and its derivatives) along with some mechanical explanation.
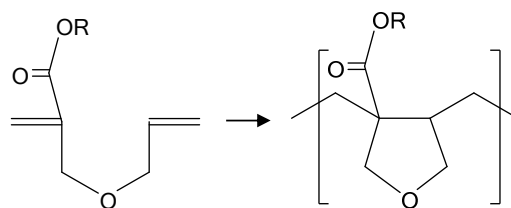
Figure 2. Polymerization of AOMA series

2. Features of cyclopolymerization

In general, non-conjugated divinyl compounds are recognized as cross-linking agents, but some may form soluble cyclopolymers consequence of alternating intra-intermolecular chain propagation. Among the known cyclopolymerization systems, most common is the radical polymerization of 1,6-dienes. Above-mentioned practical examples (Figure 1) and AOMA are correspond to this system. Intramolecular cyclization of 1,6-dienes usually produces 5- or 6-membered rings. As long as the configuration is suitable for cyclization, it may contain a bond other than a carbon-carbon bond and various functional groups, so that various ring structures can be formed. There are examples such as cyclic ethers, esters(lactones), imides, phospholics, silicones, and bicyclic compounds[1].
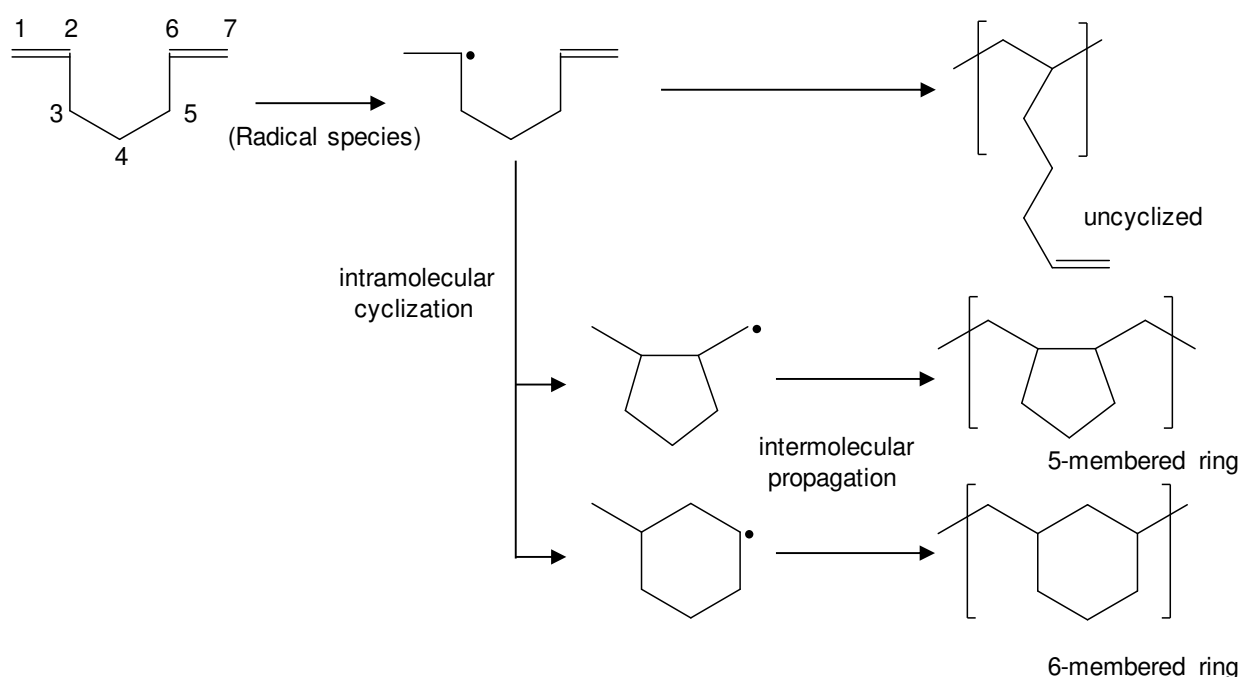

Figure 3. Typical radical polymerization of 1,6-diene

There are three types of constituting units that can be introduced into the polymer: uncyclized, 5-membered ring, and 6-membered ring. The ratio depends on the monomer structure and polymerization

conditions. Controlling the ratio of these three types, that is, controlling the number of ring members and the cyclization ratio, is a fundamental issue of cyclopolymerization, and the most important is the improvement of the cyclization ratio. It has been pointed out that the position and bulkiness of the substituent affect the number of ring members[5]. According to this, when substituents are present at both the 2- and 6-positions, the 6-membered ring tends to be formed, and 5-membered ring tends to be formed when there is no substituent either at 2- or 6-position. To improve the cyclization ratio, the basic approach is to search for appropriate monomer structure. There are mainly two approaches. The first is to suppress propagation of uncyclized chain, specifically to introduce two vinyl groups having poor polymerization reactivity. The other is the promotion of intramolecular cyclization, specifically a bulky substituent that allows the two vinyl groups to adopt a conformation that favors intramolecular cyclization. Many studies utilizing either or both of these approaches have been reported[5-9]. Monomers having a low reactive vinyl group often cause practical problem. On the other hand, monomers having a bulky substituent tend to have manufacturing and/or economic disadvantage, such as difficulty in synthesis and purification, and expensive raw materials. Therefore, it is difficult to satisfy all of the cyclization ratio, polymerization activity, and production cost. The monomers in preceding practical examples show high cyclization ratio and polymerization reactivities, and the obtained polymers exhibit a characteristic function. In the case of diallyl quaternary ammonium salts, the pyrrolidinium salt structure generated by cyclopolymerization has a unique property as a strong cationic group, and exhibits many useful functions mainly related to adsorption and dispersion. Depending on its function, diallyl quaternary ammonium salt-based polymers are used in various fields and applications such as wastewater treatment, papermaking, metal plating, dye fixation, pigment dispersion, cosmetics, antistatic, etc. In the case of the ether-type perfluoro-1,6-diene, the point is that cyclopolymerization is applied to the perfluoro resin. By introducing a cyclic ether structure into the polymer backbone, the normally crystalline perfluororesin is made amorphous. As a result, a transparent and soluble "amorphous perfluoro resin" has become industrially available, and now used in various advanced fields and applications.

3. Functional characteristics of AOMA series
3.1. Monomer structure and properties

AOMA forms a THF ring during polymerization, that is, the monomer before polymerization has a linear structure (Figure 2). In general, cyclic moiety of monomer tends to increase the viscosity (Table 1), so that acyclic AOMA series is often more advantageous than cyclic monomers in term of diluency. As shown in Figure 4, most of AOMA series have lower viscosity than (meth)acrylates of the same molecular weight. Therefore, the reactive diluent in UV curing composition is one of the most suitable uses of AOMA series.
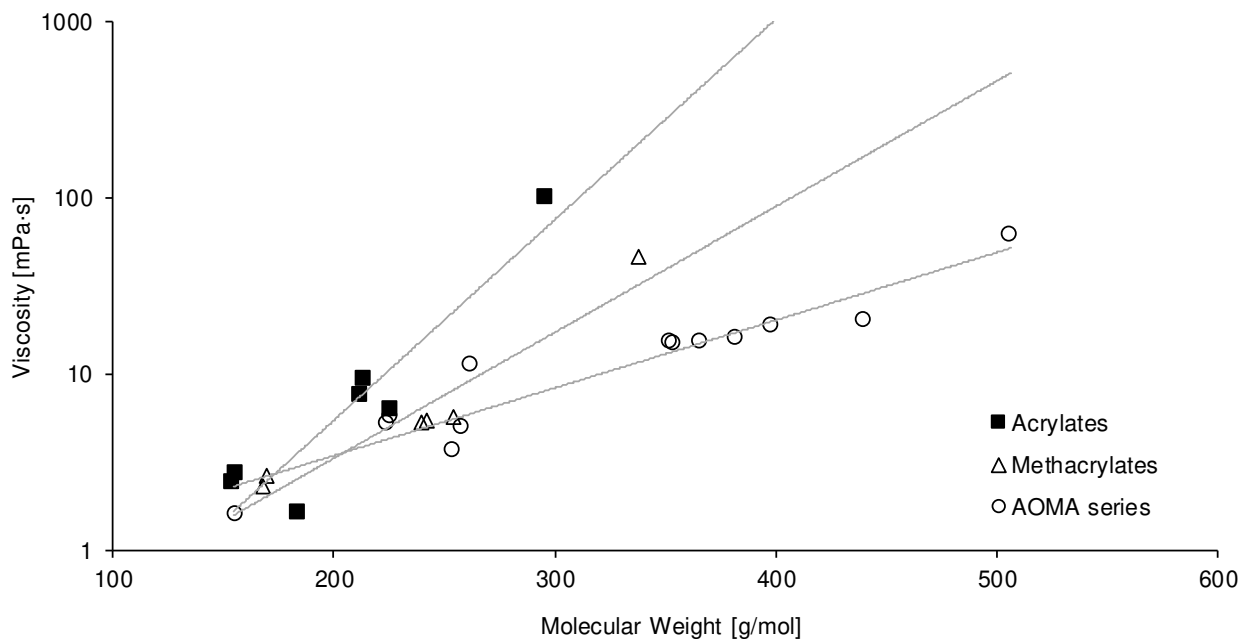
Figure 4. Viscosity of AOMA series and (meth)acrylates

3.2. Polymerization characteristics

3.2.1. Number of ring members, cyclization ratio, degree of polymerization

In radical polymerization of AOMA series, a 5-membered ring structure is formed with high selectivity among three possible structural units (uncyclized, 5-membered ring, and 6-membered ring)[10,11]. In our study, homopolymerization of AOMA in bulk results in a loosely crosslinked product which swells with solvents. On the other hands, solution polymerization results a soluble polymer in many cases. The selectivity of cyclization is generally in the upper 90%, and the degree of polymerization is at most about 100 to 150 dues to degenerative radical chain transfer derived from the allyl group. A similar tendency was observed for various AOMA derivatives we had synthesized, but it is known that the cyclization ratio of bulky tertiary esters such as *t*-butyl become almost 100%[11]. The existence of a five-membered ring structure is generally proved by spectral analysis such as NMR and observation of special physical properties that appear due to the presence of a ring. In recent years, some attempts have been made to explain this with theoretical calculations[12,13].

3.2.2. Polymerization activity

Although the growth rate constant of the α-substituted acrylate is smaller than that of (meth)acrylate, the degree of polymerization is high since the termination rate constant is also small[14,15]. AOMA series has a structure of α-substituted acrylate, polymerization reactivity is close to that of acrylate and can be polymerized under general conditions of UV curing. Figure 5 shows the results of comparing the polymerization reactivity of AOMA with (meth)acrylate using photo-DSC. Such high

reactivity is one of the evidences that AOMA polymerizes via cyclized primary radicals. However, when the initiator was decreased to 0.5 phr, the difference between THFA and AOMA became significant. We have also found that AOMA copolymerizes with common (meth)acrylates and aromatic vinyl compounds (Figure 6).
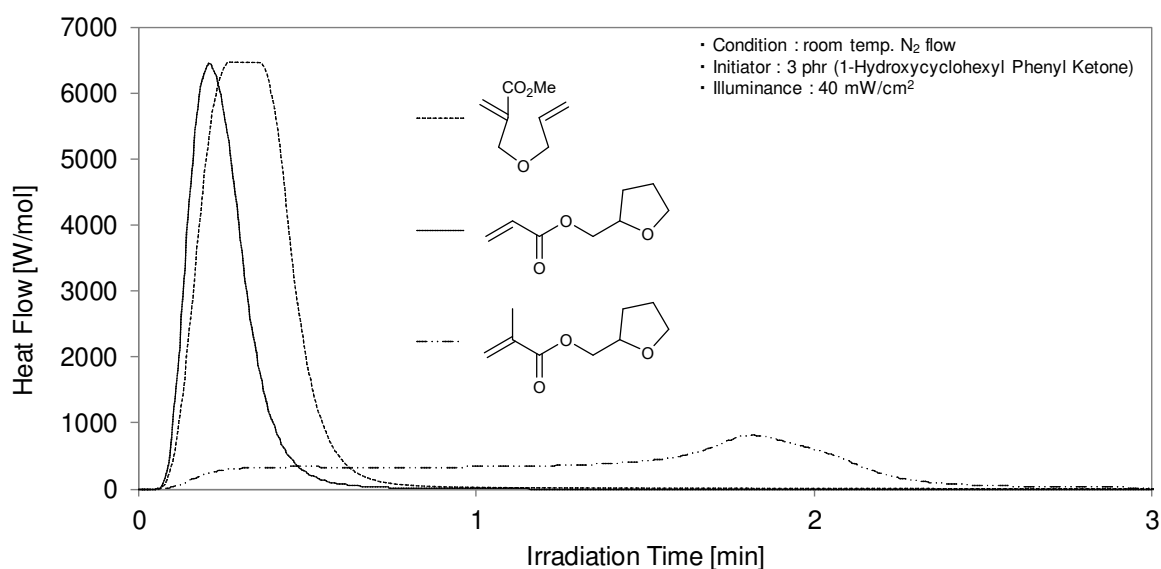

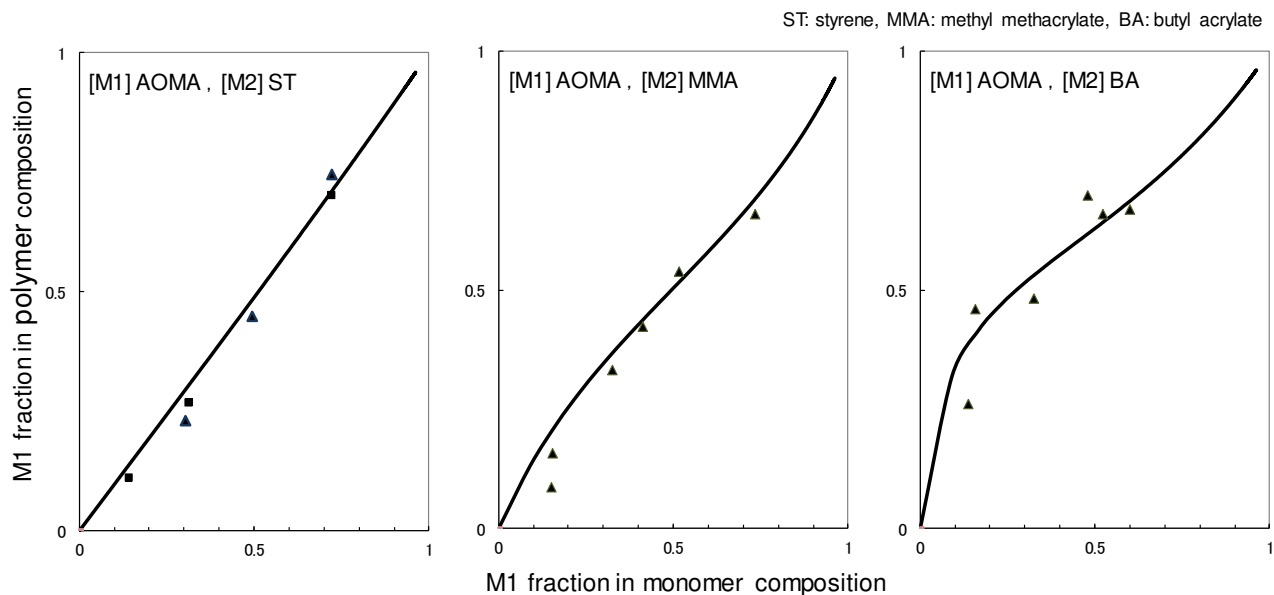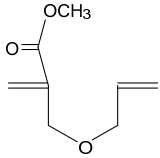**Figure 5**. Photo-DSC measurement of polymerization behavior
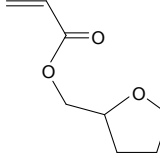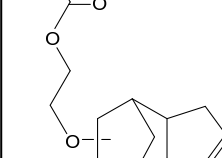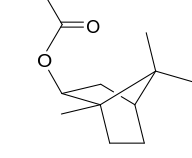

Figure 6. Copolymerizability of AOMA

3.3. Properties of main chain structure

The ring structure of the AOMA polymers exhibit many functions such as heat resistance, pigment dispersibility, substrate adhesion, and toughness. The typical characteristics are introduced below together with the mechanism.

Table 1. AOMA and commercial acrylates for comparison

Monomer	AOMA	THFA	DCPEA	IBOA
Tg [ºC]	84	-12	10 ~ 15	97
Viscosity@25ºC [mPa·s]	1.6	2.8	14.1	9.9

3.3.1. *Glass transition temperature (Tg) and the bending resistance*

AOMA series can achieve both the hardness and flexibility of polymers, which are usually in a trade-off relationship. It is considered that the rigidity is increased by having a ring structure in the main chain, while the methylene groups adjacent on both sides of the ring contribute to flexibility. Figure 7 shows the results of comparing the flexibility with Tg of the cured films composed of Trimethylolpropane triacrylate (TMPTA) and various monomers. In order to eliminate the effects of residual monomers, they were carefully cured with UV and then thermally cured.
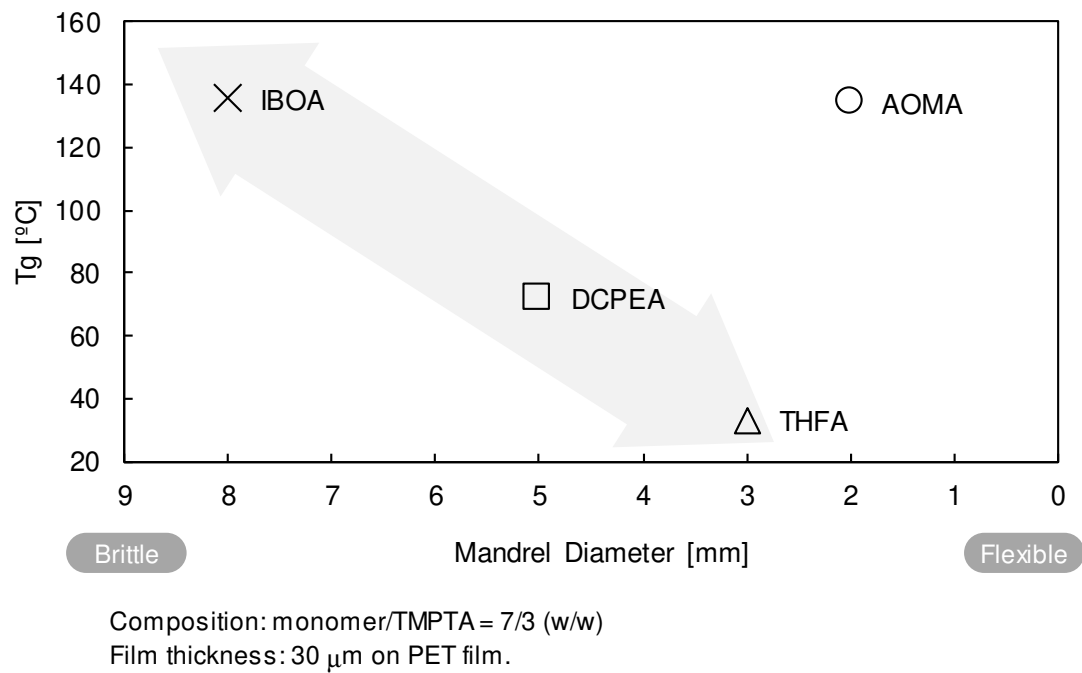
Composition: monomer/TMPTA = 7/3 (w/w)
Film thickness: 30 μm on PET film.

Figure 7. Tg and flexibility (mandrel bending test)

3.3.2. *Adhesive properties*

The strength of the adhesive is affected by interfacial interaction between the substrate and the adhesive layer, as well as the toughness and stress relaxation ability of the adhesive layer itself. In order to strongly adhere to various substrates, it is preferable that positive and negative charges are present in a well-balanced manner at the interface of the adhesive layer. Table 2 shows the results of a test on the adhesion of a UV coating film formed on a substrate using various monomers. THFA is a monomer that is useful for exhibiting almighty adhesion, but AOMA-M showed an adhesion exceeding that. It is considered that positive and negative charges existed in a well-balanced manner, and the structure brought out a toughness and a high stress relaxation ability.

Table 2. Result of adhesion test (Cross cut test: 10 x 10 pieces)

Substrate	AOMA	THFA	DCPEA	IBOA
Glass	100	67	100	18
Aluminum	100	69	100	4
PMMA	100	100	20	34
COP	32	1	77	93
TAC	100	100	2	3

- Monomer / TMPTA = 95 / 5（by weight）
　Photo Initiator ＝ 3 phr
- Thickness of cured film : 10 μm
- Numbers of undetached square from 100.

3.3.3. *Thermal decomposition / thermal coloring resistance*

It is often difficult to balance resistance to thermal decomposition and thermal coloring with other properties. For example, a bulky ring structure often introduced into a side chain for the purpose of increasing Tg is easily removed by an acid or heating. In addition, many polar groups introduced for the purpose of improving adhesion and pigment dispersibility are easily colored by heat.

Table 3 shows the results of evaluating the thermal decomposition and thermal coloring resistance by measuring the thickness and transmittance of the UV cured film of each monomer before and after heating. Although DCPEA has a good residual film ratio, thermal coloring is severe due to the influence of the double bond in the side chain. THFA and IBOA have good thermal coloring resistance at 200°C, but coloring becomes stronger under more extreme conditions. AOMA-M is highly resistant to both thermal decomposition and thermal coloring.

Table 3. Resistance for thermal decomposition and coloration

A UV-cured film of 4 to 6 μm thickness was prepared on a glass plate, and the film thickness and transmittance (400 nm) were measured before and after heating.
・monomer / DPHA = 8 / 2 (wt/wt), Initiator=3 phr
・Heating condition : (1) 200 ℃ / 30 min., (2) extra 250 ℃ / 30 min. (atmospheric conditions)

	Heating condition (1)				Heating condition (2)			
	AOMA-M	THFA	DCPEA	IBOA	AOMA-M	THFA	DCPEA	IBOA
Remaining thickness [%]	90.8	82.1	87.1	69.4	77.1	67.8	76.9	44.4
Transmittance [%]	95.9	90.8	76.9	90.8	72.7	48.2	22.0	56.5

4. Conclusions

We described the polymerization property and functional characteristics of AOMA series and its polymers. AOMA series showed low viscosity and enough reactivity suitable for UV curing application. In addition, AOMA copoymerized with conventional (meth)acrylate and styrene. THF rings on the backbone affected to the polymer property significantly, hence toughness, adhesion, and heat resistance

of the polymer was improved. Cyclopolymerizable monomers are attractive in that they can easily introduce a ring structure into the polymer, but it is difficult to achieve both performance differentiation and economic advantages over conventional monomers, so there are only a limited number of industrial applications. However, AOMA series are "easy-to-use" and the ring structure on polymer backbone exhibits various properties and is easily compatible with reciprocal properties. We are convinced that AOMA series will be utilized industrially as functional monomers in various application fields.

5. References

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