

## Free Radical-Induced Copolymerization of Norbornene and Methacrylate

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**Abstract:** Various chemically functional monomers are formatted copolymerization and feed different ratios that they affect the yield, molecular weight, glass transition temperature, and transparency. In this investigation, a series of norbornene (Nb), and methacrylate (Ma) were synthesized by catalytic amount of *N,N'*-azobis-isobutyronitrile (AIBN) as the initiator. Addition to all of these mainly properties of poly(norbornene-*co*-methacrylate)s were depended on the ratio of methacrylate (Ma)/ norbornene (Nb). Moreover, not only were glass transition temperature but also its transparency, increased with decreasing methacrylate (Ma)/ norbornene (Nb) ratios. Further, these series of targeted copolymers of compositions are identified by <sup>1</sup>H NMR spectra analyses, and calculated molecular weights approaching the end groups of main copolymers by GPC are also described in this paper. [The Journal of American Science. 2008; 4(1):90-96].

**Keywords:** Norbornene; Poly-(norbornene-*co*-methacrylate)s; *N,N'*-azobis(isobutyronitrile); Transparency

### Introduction

Optical polymers have several advantages over inorganic material in terms of lower price and opportunities [1]. However, they also have some disadvantaged properties such as modest yield of production, formatting the targeted adducts which own highly purity and lower thermal stability. Copolymerization of norbornene with ethylene leads to cycle olefin copolymer (COC) with unique physical property has been reported [2-8]. Addition to all of these products have own highly optical transparent, high glass transition temperature (T<sub>g</sub>), and high decomposition temperature (T<sub>d</sub>). Further, it potentially replaces polycarbonate on the field of engineering plastic [9-15]. Moreover, there are no polar functional groups on the skeleton of COCs, which COCs are not compatible with solvents or which the other resins [16-18]. Consequently, methacrylate serves to incorporate polar functionality into the polymer, providing necessary adhesion and solubility properties that required for optical polymer material also. In this investigation, all of these targeted polar COCs were resulting from the polymerization of norbornene (Nb) and methacrylate (Ma) using catalytic amount *N,N'*-azobis-isobutyronitrile (AIBN) as the initiator. These Poly(norbornene-*co*-methacrylate)s are typically soluble in organic solvents such as toluene, chloroform and tetrahydrofuran (THF), and that thin films have the properties of highly transparency. It is strongly believed that these optically copolymeric materials have usefully potential properties in the future.

### EXPERIMENTAL SECTION

#### General Procedures and Materials

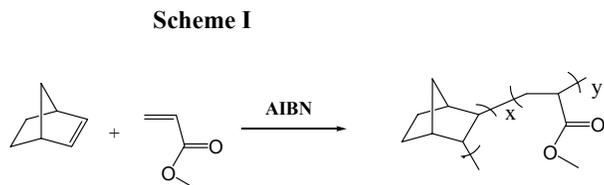
NMR spectrum was recorded on a Bruker 500MHz instrument. DSC analysis was recorded on a Perkin Elmer DSC-7 instrument. TGA analysis was recorded on a Perkin Elmer Pyris 1 instrument. Gel permeation chromatographic (GPC) analysis utilized a Polymer Standards Service column (10 μm gel. SDV linear, 60cm), a Knauer HPLC Pump 64, and a Waters differential refractometer (R 401). All GPC analyses were performed in solutions contain toluene (0.4-0.8 g/dL). Calibration was based on six polystyrene standards ranging from M<sub>n</sub> 1300 to 580000 (M<sub>w</sub>/M<sub>n</sub> < 1.1). UV-VIS spectra (HP-8453A photodiode array spectrophotometer) were measured for thin copolymers films that spin coated on glass substrates from concentrate chloroform solution. The scan range and scan rate were 200-600nm and 2nm/s, respectively; THF was dried over sodium benzophenone ketyl and distilled.

### General procedure of the polymerization reaction

The polymerization reaction was operated by adding through a Schlenk flask and charged with norbornene and mathacrylate (the molar feed ratio for norbornene to mathacrylate were 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100) and 2 mole% of *N,N'*-azobis-isobutyronitrile (AIBN), and using vacuum-transfer 10-ml THF. Under the condition of 16 hr at 70 °C, these copolymers were isolated by precipitation with methanol that products were dried over 80°C for 24 hr. In the copolymerization the molar feeds ratio for norbornene to mathacrylate were 100:0 (poly-1), 80:20(poly-2), 60:40(poly-3), 40:60 (poly-4), 20:80(poly-5), and 0:100(poly-6) gaining these targeted materials of white powder and that yield from 32% to 85% were obtained.

### RESULTS AND DISCUSSION

Copolymerization of norbornene and methylacrylate have been synthesized by using catalytic amount of *N,N'*-azobis-isobutyronitrile (AIBN) as the initiator giving random polymeric adducts were similar to the copolymer of norbornene-ethylene is shown in [Scheme I \[12-17\]](#).



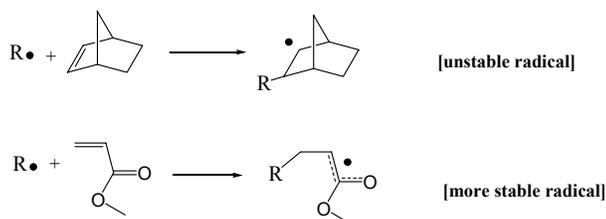
A Schlenk flask was charged with norbornene and mathacrylate (the molar feed ratio for norbornene to mathacrylate were 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100) and 2 % mole of *N,N'*-azobis-isobutyronitrile (AIBN) then added THF by vacuum-transfer. After 16 hr at 70°C, and these copolymers were isolated by precipitation with methanol giving targeted products(the molar feed ratio for norbornene to mathacrylate were, 100:0 (poly-1), 80:20 (poly-2), 60:40 (poly-3), 40:60 (poly-4), 20:80 (poly-5), and 0:100 (poly-6), dried at 80°C for 12hr. All of these results of the experiments are summarized in [Table 1](#) also.

### Composition of norbornene and mathacryl- ate copolymer

Poly-3 has strongly peak of chemical shift at  $\delta$  3.7-3.4 ppm for three methyl protons and chemical shift at  $\delta$  2.3-0.8 ppm for three ethylene protons, and ten norbornene protons with the ratio of 1:2.14 integral also. This result indicates that the copolymeric composition is 27:73 for norbornene to mathacrylate that it is shown in [Fig. 1](#). Additionally, the copolymerization of the molar feeds ratio for norbornene to mathacrylate were 80:20, 60:40, 40:60, and 20:80. The composition of the obtaining Poly(norbornene-*co*-methacrylate)s were founded 37:63, 27:73, 18:82, and 9:91 for norbornene to mathacrylate repeat unit in basing on the analysis of <sup>1</sup>H NMR spectra that is shown in [Table 1](#).

Consequently, according to <sup>1</sup>H-NMR spectra analysis, the composition of Poly-(norbornene-*co*-methacrylate)s is increased by the ratios of methacrylate/ norbornene. In 1971, Koch and Gleicer reported that bridged allylic hydrogen on the norbornene did not have chain-transfer in appreciable extent due to the resulting unstable radical[18]. On the other hand, mechanically, as the methacrylate has own an ester of electron-withdrawing group which radical is stabilized of delocalization, and that is shown in [Scheme II](#).

**Scheme II**



**Number-averaged molecular weights and yields  
of the copolymeric methacrylate/norbornene materials**

These copolymers associate with number-average molecular weight ranging from 6000 to 29000 (Mw/Mn from 1.43 to 2.69), and 32%~85% yields were typically obtained. An increase in methacrylate monomer feeds ratio resulting in an increase in the number-average molecular weight. However, a simultaneous increase in yield was also observed for poly-1 (polynorbornene), and poly-6 (polymethacrylate) [19] that are shown in Table 1.

Poly-1 (PNB:Polynorbornene) was synthesized in higher yield (71.5%) and broader Mw/Mn (2.69) from the rigid property of structure and higher number-average molecular weight (28878) from bridged allylic hydrogen property.<sup>18</sup> On the other side, poly-6 (PMA : Polymethacrylate) was synthesized in modest yield (42%) and higher number-averaged molecular weight (27307) from the softly structural property and lower molecular weight; it was also soluble in methanol.

The <sup>1</sup>H NMR chemical shift of poly-3 shows peaks at  $\delta$  6.15 ppm and  $\delta$  5.93 ppm with the ratio of 1:1 integral. It is assigned to the  $C=CH_2$ , that is the end group of Poly-3, and that it is shown in Fig. 1. There are two protons in the end group and three methyl protons with the ratio of 2:236.4 integral. Consequently, this result is calculated that the number-averaged molecular weight showing 9505 for the copolymer and approximate GPC experimental value 9461.

**Thermal and optical properties of methacrylate and norbornene Copolymer**

Those analyses of differential scanning calorimetry (DSC) were shown that the glass transition temperature (Tg) of copolymers fall in the region of 142.3~28.8°C, which it is shown in Fig. 2. Additionally, as methacrylate has soft structure that is an increase in monomer of methacrylate feeding ratio resulted in a decrease in the glass transition temperature (Tg). Moreover, Fig. 3 shows the decomposition temperature (Td) by thermogravimetric analysis (TGA). The decomposition temperature (Td) of the copolymer was around 360-388°C, and monomer feed ratio was not significant.

Thus, the copolymer of thin films of the UV absorption spectra is showed in Fig. 4. Consequently, in the range of 300-600 nm that is an increase in methacrylate monomer feeding ratio and resulted in a decrease in the transparency that is shown in Table 1. Typically, thin films were spin-coated on 1x1cm quartz substrate and film thickness which was controlled 500±20 nm that transparence are around 7-60% at 220 nm. Poly-6 is methacrylate homopolymer (PMA : Polymethacrylate), and that only transparence 7% at 220 nm. Last, but no means least, methacrylate is an unsaturated molecule containing carbonyl group undergo  $n \rightarrow \pi^*$  (ca. 205nm) transition [20]. In a word, norbornene homopolymer (Poly-1 ; PNB : Polynorbornene) does not contain unsaturated functional group which means it has highly transparence 60% at 220 nm.

## CONCLUSIONS

To sum up, the materials of polar COCs were synthesized in this work that the targeted copolymer of properties are not only highly transparent, decomposition, and temperature, but they also they are readily soluble in organic solvent, such as toluene, methylene chloride, as well as tetrahydrofuran. In addition, the synthetic monomer feed ratio that affect the yield, molecular weight, glass transition temperature, transparency and composition of copolymer of norbornene and methacrylate have been investigated for free radical reaction. Consequently, the composition of copolymer is identified from <sup>1</sup>H NMR spectra analysis and the calculated molecular weights approach by GPC analysis from the end group. Last, but not means the least, the copolymer of the effort has indicated that yields, molecular weights, and compositions are resulting in increasing the ration of methacrylate (Ma) and norbornene (Nb). In a word, the glass transition temperature and transparency increased with decreasing methacrylate (Ma)/ norbornene (Nb) ratio are described in this publication.

**Table 1. Norbornene(Nb)/Methacrylate(Ma) Copolymerizations were catalyzed by AIBN<sup>a</sup>**

NO molar Nb/Ma <sup>c</sup>	feed molar transparency ratio Nb/Ma (%) <sup>d</sup>	yield (%)	Tg(°C)	Td(°C) <sup>b</sup>	Mn	Mn/Mw	copolymer ratio	
Poly-1	100/0	71.5	142.3	380	28878	2.68	100/0	60
Poly-2	80/20	32	96.7	367	6441	1.43	37/63	54
Poly-3	60/40	53	71.3	387.9	9461	1.98	27/73	48
Poly-4	40/60	71	41.3	370.7	16310	2.02	18/82	38
Poly-5	20/80	85	28.8	366.9	27742	2.01	9/91	12
Poly-6	0/100	42	29.4	360.5	27307	1.83	0/100	7

<sup>a</sup> Conditions: AIBN = 2 mol%, T = 70°C, solvent = THF. <sup>b</sup> 95% weight lose. <sup>c</sup> for <sup>1</sup>H NMR spectra analysis. <sup>d</sup> film thickness

was controlled 500±20nm and transparent at 220 nm.

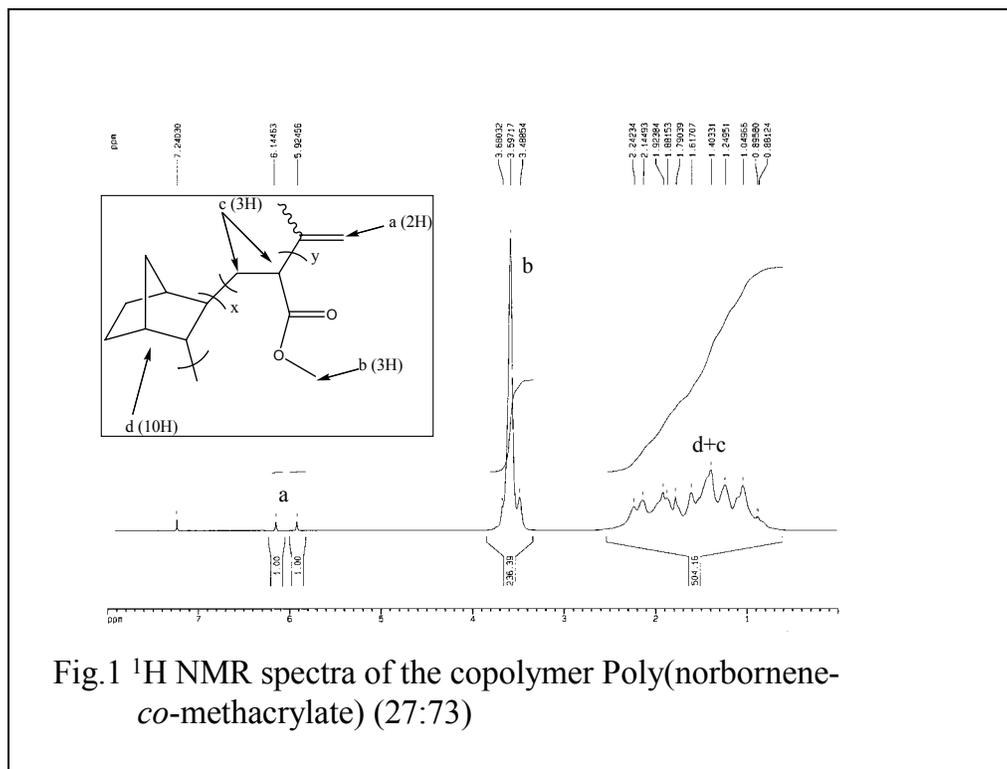


Fig.1  $^1\text{H}$  NMR spectra of the copolymer Poly(norbornene-*co*-methacrylate) (27:73)

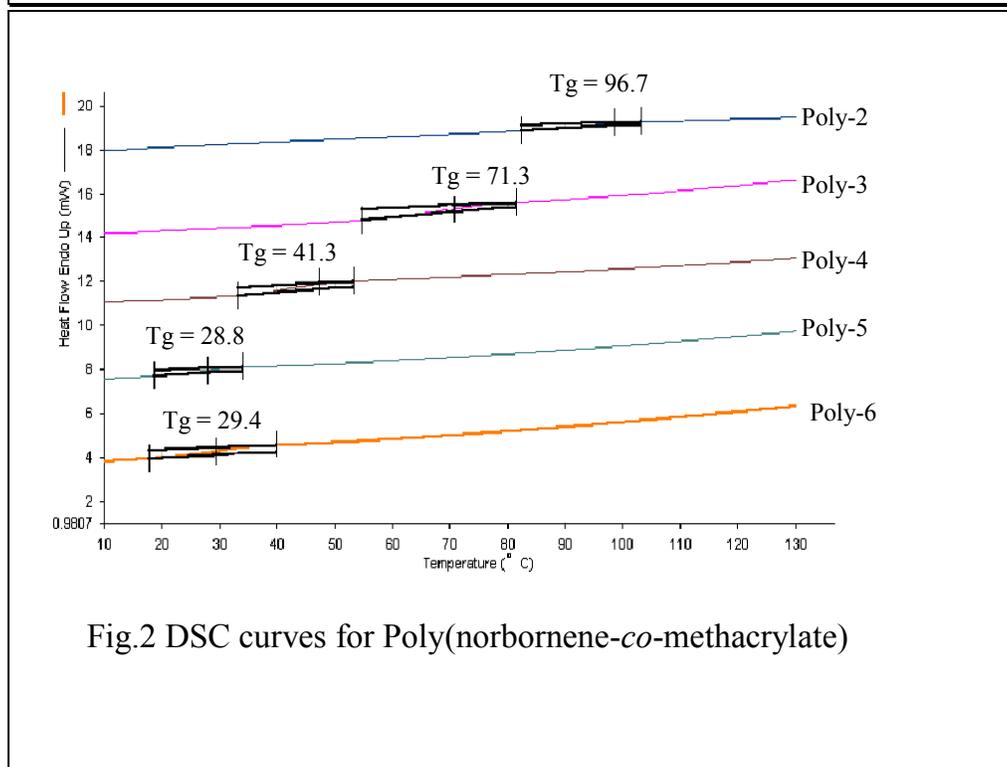


Fig.2 DSC curves for Poly(norbornene-*co*-methacrylate)

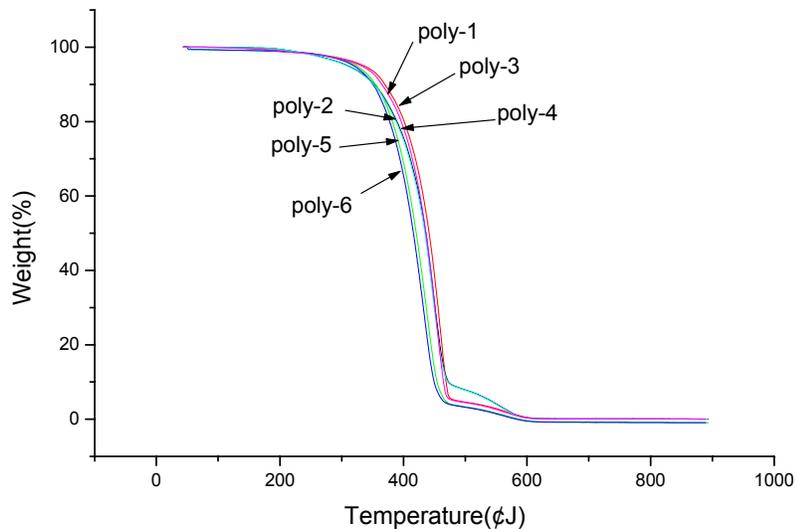


Fig.3 TGA curves for Poly(norbornene-*co*-methacrylate)

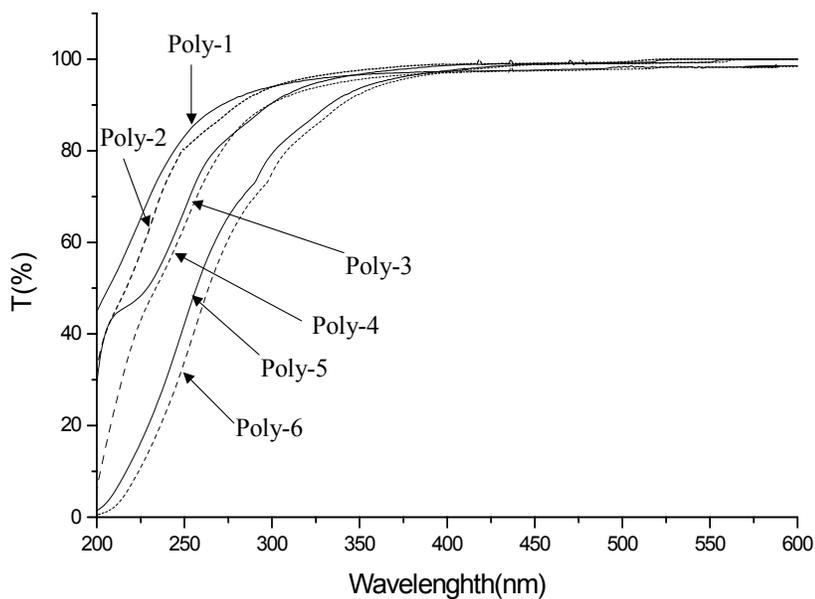


Fig.4 UV absorption spectra of the Poly(norbornene-*co*-methacrylate)s' thin films.

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