Preparation and Properties of Ester or Cyano Group Substituted Ring-Opening Polymers and Their Hydrogenated Derivatives

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ABSTRACT: Ester or cyano substituted tetracyclo[$4.4.0.1^{2,5}.1^{7,10}$]dodec-3-enes (**1**) were synthesized and their metathesis ring-opening polymerization was examined. The tungsten-based ternary catalyst system polymerized them very well. The polymers showed high glass transition temperatures (T_g) and no evidence of crystallization (e.g, the T_g of the polymer derived from 8-methyl-8-methoxycarbonyl substituted monomer (**1a**) was 207°C, and colorless transparent films could be casted from the solution of the polymer). The stability of these high T_g polymers were too unstable, so practical thermal molding methods could not be applied to them. The hydrogenation of these polymers with a palladium catalyst decreased T_g and greatly increased thermal stability. The physical and thermal properties of the hydrogenated polymers were thoroughly investigated. Monomer **1** was successfully copolymerized with other cyclic olefins. The resultant copolymers were hydrogenated, giving thermally stable polymers. In all cases examined in this study, a decrease of T_g by hydrogenation was about 35°C, regardless of the monomer structure. These results indicate that the main-chain mobility is the major contribution to the decrease of T_g. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 367–375, 1997

Key words: ring-opening polymerization; metathesis; hydrogenation; glass transition temperature; transparent resin; thermal stability

INTRODUCTION

Metathesis ring-opening polymerization has attracted great attention for years because of its unique polymerization mode.[1,2] It has been shown that various types of cyclic olefins can be polymerized. One of the interesting features is that a certain selection of the catalyst system enables us to polymerize cyclic olefins bearing polar substituents.[3–10] Another characteristic is the introduction of an alicyclic structure into the polymer main chain, which leads to high T_g.[11,12] Compared to these polymers having aromatic rings in their main chain, one can expect that the alicyclic polymers would be more optically homogeneous because of the absence of resonanced p-orbitals and a lower tendency to crystallize. Despite these promising features, there are very few reports concerning the thermal and physical properties of the metathesis polymers except for several commercialized polymers such as *trans*-poly(1-pentenylene),[13–15] *trans*-(poly(1-octenylene),[16] and polymers of norbornene.[17,18] In 1977, some reports and patents appeared mainly concerning the polymers containing 5-cyanonorbornene units.[11,12] Although many types of polymers were disclosed, detailed properties are still ambiguous. In this report, we describe the metathesis ring-opening polymerization of 8-alcohoxycarbonyltetracyclo-[$4.4.0^{1,2}.1^{7,10}$]dodec-3-enes (**1**) and 8-cyano deriv-

ative (**1g**) and copolymerization with other poly-cyclic olefins. Thermal and physical properties of the resultant polymers were examined.

As already having been pointed out, these ring-opened polymers have poor thermal stability due to the unsaturation.[19,20] Therefore, some of the polymers were hydrogenated and their properties were closely examined.
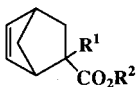
The bulky polycyclic monomers are expected to give rise to new polymers that would have high T_gs and show good transparency because the bulky and unsymmetrical polycyclic structure in the main chain would prevent crystallization.
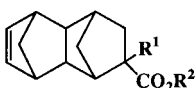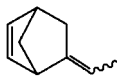

1a : R^1 = Me, R^2 = Me
1b : R^1 = H, R^2 = Me
1c : R^1 = Me, R^2 = Et
1d : R^1 = Me, R^2 = n-Bu
1e : R^1 = Me, R^2 = t-Bu
1f : R^1 = Me, R^2 = C$_6$H$_{11}$
1g : R^1 = H, R^2 = CN
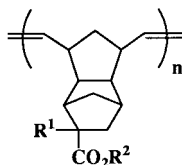
Poly-1a ~ 1g

2a : R^1 = Me, R^2 = Me
2b : R^1 = H, R^2 = Me
2g : R^1 = H, R^2 = CN

ENB

Poly-1a, 1c $\xrightarrow[\text{Pd}]{\text{H}_2}$
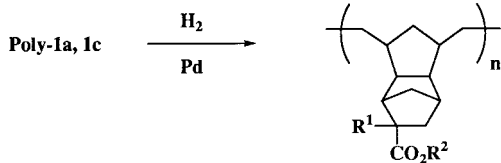
Poly-3a, 3c

EXPERIMENTAL

Materials

8-Methyl-8-methoxycarbonyltetracyclo-[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene (**1a**) was synthe-sized by double Diels-Alder reaction of cyclopen-tadiene and methylmethacrylate. Commercially available dicyclopentadiene and equal mole of

reagent grade methyl methacrylate were put in an autoclave and heated for 9 h at 175°C. The resulting mixture was separated by careful frac-tional distillation. **1a** was obtained 10% yield (99.5% purity by GC analysis, bp 102°C/0.6 mmHg).

Other polycyclic monomers were prepared in the same way from dicyclopentadiene and corresponding alkylmethacrylates or methyl acrylate. They included 8-methoxycarbonyl-tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene (12%, yield, bp 115–120°C/0.6 mmHg, **1b**), 8-methyl-8-ethoxycarbonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene (10% yield, bp 104°C/0.6 mmHg, **1c**), 8-methyl-8-n-butoxycarbonyltetracyclo-[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene (11% yield, bp 118–124°C/0.3 mmHg, **1d**), 8-methyl-8-t-butoxycar-bonyltetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene (6% yield, bp 120–130°C/0.3 mmHg, **1e**), and 8-methyl-8-cyclohexyloxycarbonyltetracyclo-[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene (12% yield, bp 150–153°C/0.3 mmHg, **1f**). 8-Cyanotetracyclo-[4.4.0.1^{2,5}.1^{7,10}]dodec-3-ene (**1g**) was obtained from acrylonitrile and dicyclopentadiene in 17% yield, bp 142–149°C/5 mmHg. Although all these monomers were obtained as isomeric mixtures, no effort to separate them was made.

4-Ethylidenenorbornene was dried over molec-ular sieves (type 4A) under nitrogen. 4-Methyl-4-methoxycarbonylbicyclo[2.2.1]hept-1-ene (**2a**) was prepared as described in the literature.[11]

Hexachlorotungsten was dissolved in chloro-benzene at a concentration of 0.05 mol/L. Diethyl-aluminumchloride was purchased as a 15% (w/w) solution in n-hexane and used as 1.0 mol/L solution diluted with n-hexane. Paraldehyde was used as a 0.1 mmol/L solution of 1,2-dichloroe-thane. Palladium/alumina [5% (w/w)] was ob-tained commercially and used as received.

All the solvents and 1-hexene were dried over molecular sieves (type 4A) under nitrogen.

Polymerization

Poly-1a

In a 100 mL flask purged with dry nitrogen fitted with a stirrer were placed 10 g (43 mmol) of **1a**, 1,2-dichloromethane (30 g), and 1-hexene (0.72 g, 8.6 mmol). In another flask, the solution of the hex-achlorotungsten and paraldehyde was mixed in 1/1 molar ratio. To the flask containing the monomer, 0.17 mL of diethylaluminumchloride solution was added followed by addition of 0.26 mL of the tung-

Table I Polymerization of 1 and 2[a]

Monomer	R^1	R^2	Monomer/WCl$_6$ (mol ratio)	Al/W[b] (mol ratio)	1-Hexene (mol %)	Yield (%)	η_{inh} (dL/g)	T_g[c] (°C)
1a	Me	Me	5000	20	20	98	0.84	207
1b	H	Me	500	5.8	20	29	0.80	206
1c	Me	Et	5000	20	20	93	0.73	160
1d	Me	n-Bu	500	8.6	20	92	0.84	100
1e	Me	t-Bu	2000	10	20	82	0.86	> 240
1f	Me	c-C$_6$H$_{11}$	500	8.6	10	11	0.38	127
1g	H	CN	500	6.0	0	59	—	> 240
2a	Me	Me	500	10	2.0	92	0.64	82
2b[d]	H	Me	500	10	1.0	—	3.16[e]	62
2g[d]	H	CN	500	10	1.0	—	0.66[e]	140

[a] All polymerization was performed at 60°C for 3 h.
[b] The molar ratio of Et$_2$AlCl and WCl$_6$. Paraldehyde/W = 1 (molar ratio).
[c] Measured by DSC.
[d] Data from reference 11.
[e] Measured in toluene at 30°C.

sten and paraldehyde solution. The mol ratios of **1a**/ tungsten and aluminum/tungsten were 5000 and 20, respectively. Then the flask was heated 60°C for 3 h. The resulting viscous solution was poured to a large amount of methanol with vigorous stirring. The obtained white powder was dried at 80°C under vacuum. The inherent viscosity of the polymer was 0.70 dL/g, measured at a concentration of 0.5 g/dL in chloroform at 30°C. The infrared (IR) spectrum (KBr tablet) exhibited a carbonyl absorption at 1735 cm^{-1} (C=O). The ^{1}H-NMR spectrum (CDCl$_3$) showed absorption at 3.64 ppm (singlet, MeO) and 5.41 ppm (broad singlet, vinyl) in a ratio of 3/2.

All other polymers were prepared by similar procedure as described above.
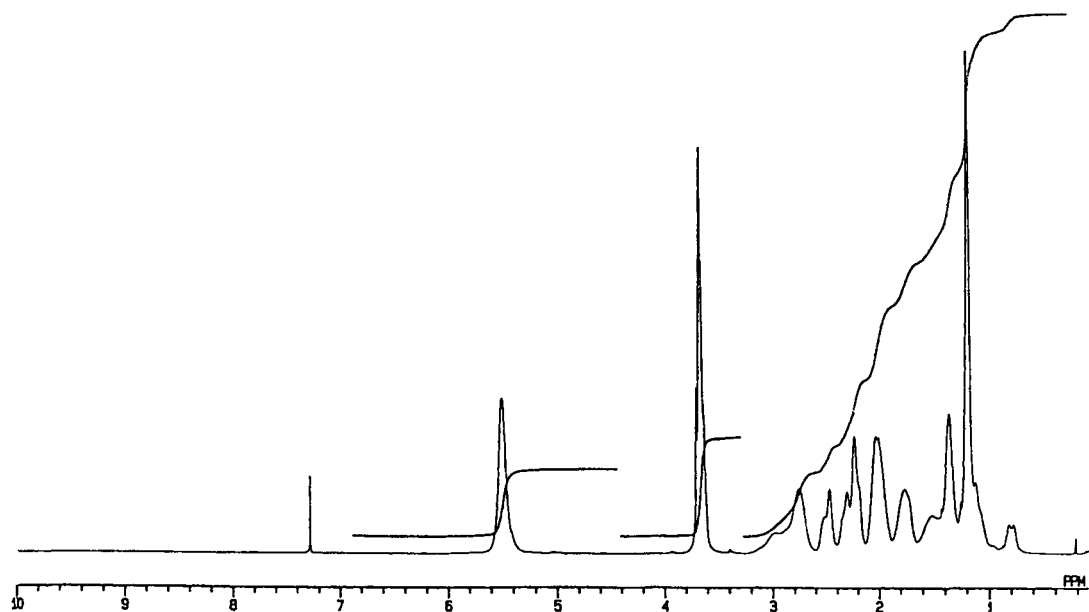
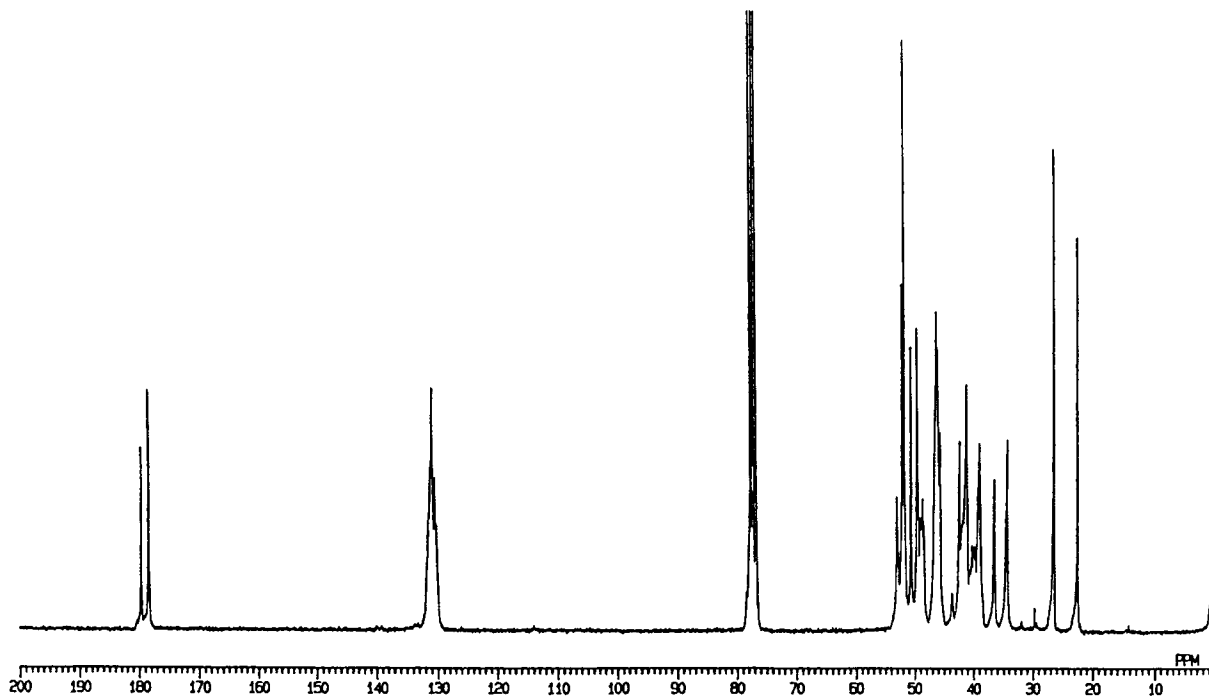**Figure 1** ^{1}H-NMR (270 MHz) spectrum of **poly-la**.

Figure 2 ^{13}C-NMR spectrum of **poly-la**.

Hydrogenation

Hydrogenation of poly-1a

In a 2 L autoclave were placed with 500 g of THF solution (10 wt %) of **poly-1a** and 10 g of palladium/alumina. The mixture was stirred under the 40 kg/cm^2 of hydrogen and heated to 165°C for 4 h. The resultant solution suspended with black catalyst was filtered. The clear polymer solution was poured into a large amount of methanol to separate the polymer. The white powder was dried at 80°C under vacuum. The ^{1}H-NMR spectrum (CDCl$_3$) exhibited absorption at 3.64 ppm (singlet, MeO) but no vinyl absorption was detected. All other hydrogenated polymers were prepared by similar procedure.

For the evaluation of properties, ring-opened polymer samples were prepared by using a 50 L stainless steel autoclave and recovered by steam distillation of the volatile materials. Hydrogenation was performed using 100 L high-pressure autoclave.

Measurements

IR spectra were recorded on a JSCO IR-810 spectrometer. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed with Seiko I&E DSC20 and TG/DTA20, respectively. UV-VIS spectra were recorded on a HITACHI U-

3210 spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were measured on a JEOL FX-100 and EX-270 Fourier transform spectrometer. The degree of the hydrogenation was determined by comparing the intensity of the vinyl hydrogen relative to that of
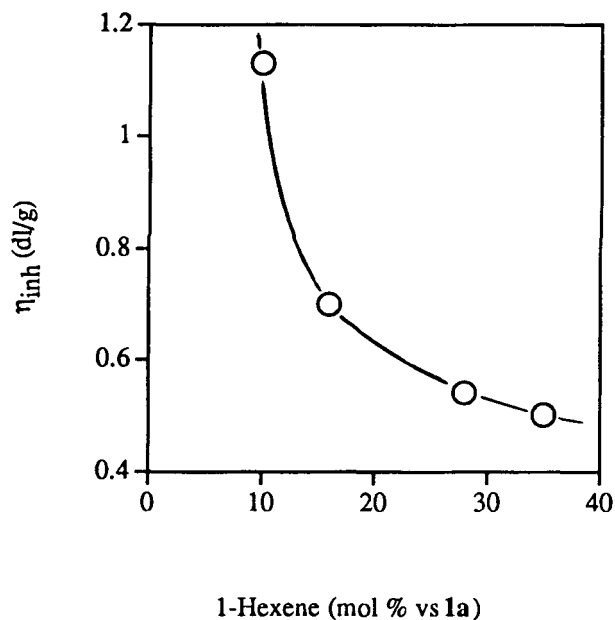

1-Hexene (mol % vs 1a)

Figure 3 Control of the molecular weight of **2a** by 1-hexene.

Table II   Copolymerization of 1a with ENB and 3a[a]

Copolymer	Comonomer (wt %)			Yield (%)	η_{inh} (dL/g)	T_g (°C)
	1a	**ENB**	**3a**			
1a/ENB (95/5)	95	5	—	91	—	184
1a/ENB (90/10)	90	10	—	91	—	179
1a/ENB (80/20)	80	20	—	92	—	158
1a/2a (95/5)	95	—	5	94	0.59	194
1a/2a (80/20)	80	—	20	88	0.52	175
1a/2a (60/40)	60	—	40	80	0.58	135

[a] Monomr/WCl$_6$ = 5000 (mol ratio), Et$_2$ AlCl/WCl$_6$ = 20 (mol ratio), and paraldehyde/WCl$_6$ = 1 (mol ratio).

methyl (**poly-1a**) or methylene (**poly-1c**) hydrogens of ester group using EX-270 (270 MHz).

For the measurement of the physical properties, polymers were injection molded to pieces of specified size. Measurements were made by the standard procedures.

RESULTS AND DISCUSSION

Polymerization of 1 and Copolymerization of 1a

As shown in the previous article, a tungsten-based ternary catalyst system exhibited good activity to the polymerization of **1**.[11,12] The results are summarized in Table I. These polymers were analyzed by IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. The presence of two vinylic hydrogens and two allylic hydrogens shown in the ^{1}H-NMR spectrum in Figure 1 clearly supports ring-opened structure of **poly-1a**. The vinylic hydrogens gave only a broad singlet and lead no information about the configuration of the double bond. Figure 2 shows ^{13}C-NMR spectrum of **poly-1a**. The presence of two distinct signals of carbonyl carbon (178.18 and 179.44 ppm) and methyl carbon attached to the norbornene ring (26.47 and 22.48 ppm) in the ratio of 57/43 indicates that two major isomers of the starting compounds have retained their structure throughout the polymerization,[21] although the configuration of the formed double bonds are thought to be a mixture of *cis*- and *trans*-isomers. IR spectra of **poly-1a** exhibits two signals at 980 and 760 cm^{-1}, corresponding to the out-of-plane stretching of vinyl hydrogen of the *trans* and *cis* double bond, respectively. The *trans* absorption was slightly stronger than *cis*, and the ratio was 66/34. This value falls in a range of what has been observed for the "classical" tungsten catalyst system.[22–24] Presence of exo-endo and syn-anti-isomers in the starting compounds prevented

us from further investigation on the microstructure of the polymer.

The T_gs of the **poly-1** are significantly higher than corresponding polymers derived from ring-opening polymerization of bicyclo[2.1.0]hept-2-enes (**2**) as shown in Table I. For example, the differences of T_g between **poly-1a** and **poly-2a**, and **poly-1b** and **poly-2b** are more than 100°C. The methyl group at the carbon attached with the carbonyl group gave a rise of practically no effect on the T_gs of the polymers derived from tetracyclo[4.4.0.1^{2,5}.1^{7,10}]dodecenes (**poly-1a** and **poly-1b**), whereas it raises about 20°C for the polymer from monomer **2** (**poly-2a** and **poly-2b**). Although the mobility of the relatively flexible cyclopentane ring is affected by methyl substitution, the substitution on the rigid bicyclo[2.2.0]-heptane structure has little effect on the T_g. It is interesting to note that the alkyl chain length of the ester moiety resulted in a considerable decrease of T_g (**poly-1a, -1c,** and **-1d**), even though the main chain of the polymer is constructed with a bulky and rigid tricyclic structure. We regard this as a plasticizing effect of the hydrocarbon chain. It is known that introduction of a nitrile group can cause an upward shift of T_g.[11] The same effect was observed in these polymers; thus, the

Table III   Hydrogenation of Poly-1a, -1c and Copolymers

Polymer	Hydrogenation Degree (%)	T_g (°C)	ΔT_g[a] (°C)
Poly-1a	> 99.9	173	34
Poly-1c	99.6	130	30
Poly-1a/ENB (95/5)	> 99.9	149	35
Poly-1a/2a (80/20)	> 99.9	141	34

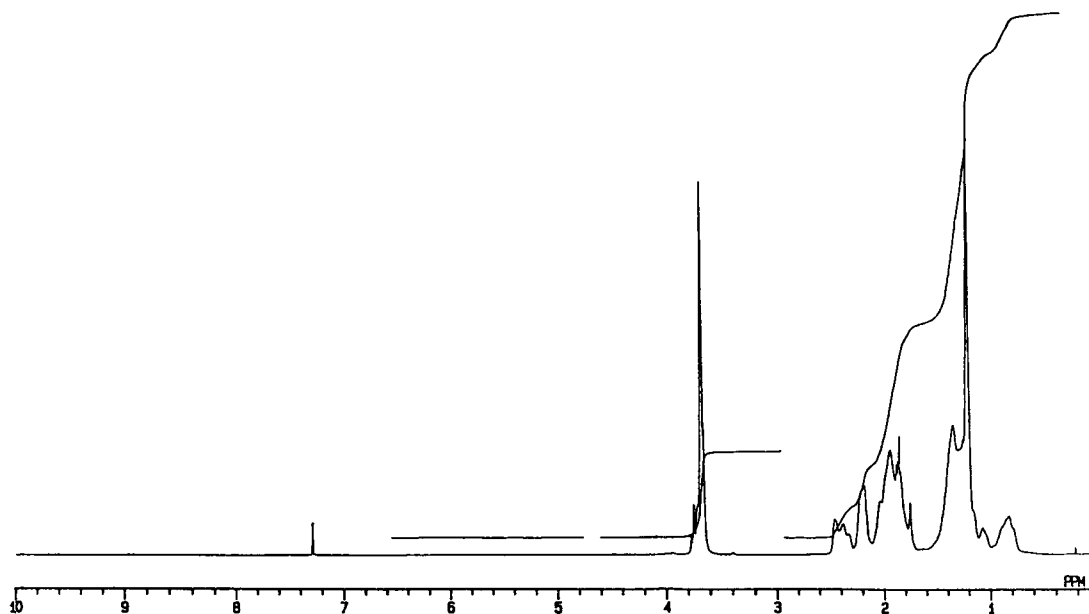[a] Difference of T_g before and after hydrogenation.

Figure 4 ^{1}H-NMR spectrum (270 MHz) of hydrogenated **poly-la** (**poly-[1a − H$_2$]**.

T_g of **poly-1g** was so high that it could not be measured because its decomposition (presumably gelation) had occurred over 240°C. The T_g of the *t*-butyl-substituted polymer, **poly-1e**, could not be determined either for the same reason. Accordingly, bulky *tert*-butyl substituent shows no plasticizing effect.

It is necessary to have several kinds of polymers with various molecular weights and various T_gs for different applications. A molecular weight of **poly-1a** was easily controlled by addition of 1-hexene without affecting the polymer yield (Fig. 3).

The T_g of **poly-1** can be adjusted by copolymerization with a less rigid monomer. For this purpose, industrially available 4-ethylidennorbornene (**ENB**) and **2a** were selected as a comonomer. Incorporation of **ENB** up to 20 wt % decreased the T_g of the resultant polymer from 207 to 158°C (Table II). Copolymerization of **2a** with **1a** was also effective; nevertheless, the polymer yield slightly decreased because of poor reactivity of **2a**.

Hydrogenation of poly-1a, poly-1c, and Copolymers and Their Properties

As expected, **poly-1** and copolymers are too thermally unstable to be processed as a conventional thermoplastic. A relatively low T_g polymer, **poly-1d**, also showed the tendency to discolor by heat. Thermal instability of the polymer is largely due

to the unsaturation of the main chain, so **poly-1a** and **poly-1c** and copolymers of **1a** were hydrogenated. Hydrogenation reaction was catalyzed by palladium/alumina under 40 kg/cm^2 of hydrogen pressure. The results are summarized in Table III. ^{1}H-NMR spectrum of the hydrogenated polymer of **poly-1a** (**poly-[1a + H$_2$]**) showed no vinyl hydrogen signals and allylic hydrogens at 2.3–3.2 ppm (Fig. 4). The fact that the chemical shift of the methyl group attached to the norbornane ring shows no change indicates that the
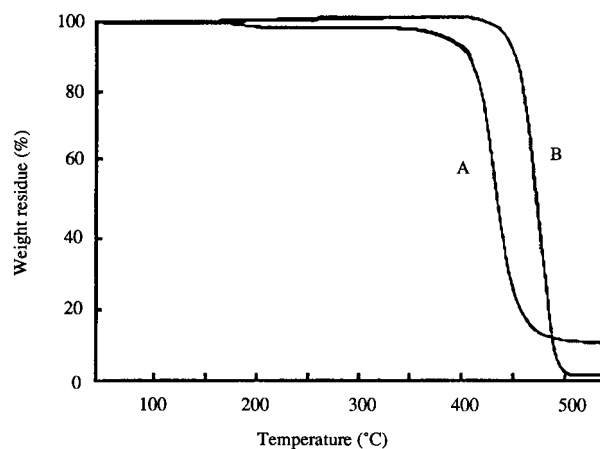

Figure 5 T_g curves for **poly-la** (A) and **poly-[1a + H$_2$]** (B) measured under nitrogen. Temperature was raised at a rate of 10°C/min.
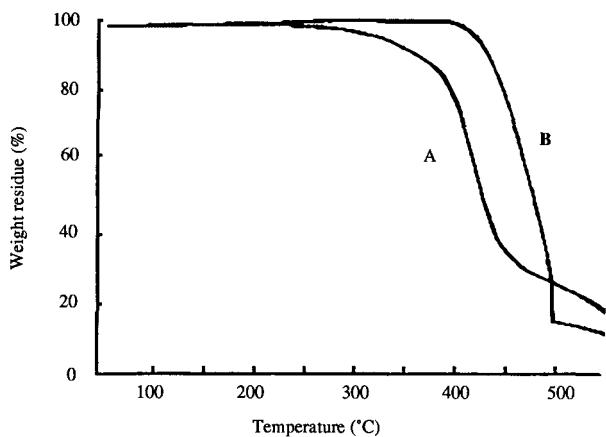
Figure 6 T_g curves for **poly-1a** (A) and **poly-[1a + H$_2$]** measured under air. Temperature was raised at a rate of 10°C/min.
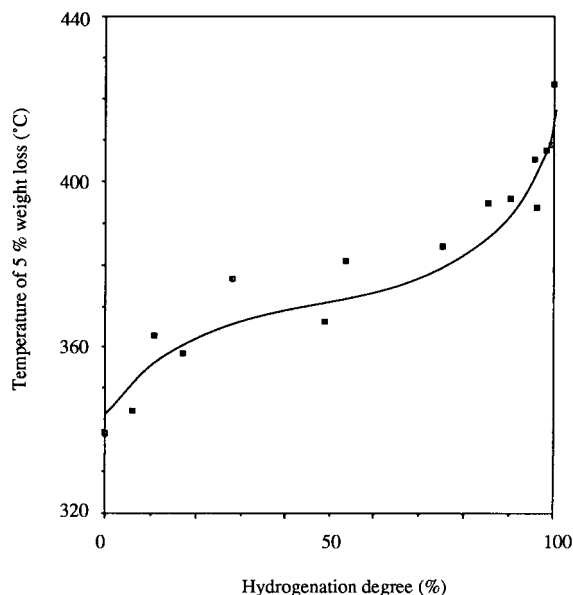

Figure 7 Dependence of thermal stability of **poly-1a** against hydrogenation degree. Plot of 5% weight loss temperatyure against hydrogenation degree.

polycyclic ring structure remains intact. Moreover, there was no evidence of decomposition of the ester group. Saturation of the double bond decreased the T_g considerably. Obviously, the rotation around the hydrogenated carbon–carbon single bond made the mobility of the polymer chain easier. There was no evidence of crystallization in contrast to the hydrogenated polynorbornene derivatives, which has been reported to have melting temperature at a high hydrogenation degree.[25,26] The amorphous nature of the hydrogenated polymers is due to the stereorandomness of the starting monomer and unsymmetrical structure of the resultant polymer. Copolymers of **1a** and **ENB** or **1a** and **2a** were also successfully hydrogenated under the same condition. It is interesting that the decrease of T_g incurred by saturation of the double bond is about 35°C, regardless of substituent of ester moiety or comonomer. A similar decrease in T_g was observed for the hydrogenation of the ring-opened polymer of dicyclopentadiene.[19] In this case, the T_g dropped 41°C. The difference of T_gs between polyethylene[27] and polybutadiene[28,29] is also around 30–40°C. In all these results it is understood that the decrease of the

T_g upon hydrogenation mostly originats from the mobility change of the polymer main chain.

The improvement of the thermal stability of the polymer was significant. The stability was evaluated by TG in air or nitrogen atmosphere. Figures 5 and 6 show the TG curves for **poly-1a** and **poly-[1a + H$_2$]**, and Table IV summarizes their 5% weight loss temperatures. Saturation of the double bond lead about an 80°C increase of decomposition temperature both under air and nitrogen. The degree of the hydrogenation plays a very important role for the improvement of the thermal stability. Figure 7 shows the effect of the hydrogenation degree on the 5% weight loss temperature of the polymers prepared from **poly-1a**. Although the increase of the thermal stability is moderate, less than 80% of hydrogenation degree, the stability is improved drastically as the hydrogenation approaches 100%. This result indicates that the polymer needs to be hydrogenated as completely as possible to give the most thermally stable resin.

The hydrogenated polymer **poly-[1a + H$_2$]** can easily be molded by injection molding or hot press. Table V summarizes the physical properties of **poly-[1a + H$_2$]**. The values of the polymethylmethacrylate (PMMA) and polycarbonate (PC) are included for the sake of comparison. **Poly-[1a + H$_2$]** has good tensile and flexural properties and Izod impact strength comparable to the PMMA.

Table IV   Thermogravimetric Analysis of Poly-1a and Poly-[1a + H$_2$]

	5% Weight Loss Temperature	
Polymer	Under Air	Under Nitrogen
Poly-1a	339	378
Poly-[1a + H$_2$]	423 ($\Delta T = 84$°C)	446 ($\Delta T = 68$°C)

Table V   Physical Properties of Poly-3a

Properties	ASTM	Unit	Poly-[1a + H$_2$]	PMMA	PC
Mechanical properties					
Tensile strength	D638	kg/cm^2	750	700	640
Tensile elongation	D638	%	16	10	120
Flexural strength	D790	kg/cm^2	1100	1100	1000
Izod impact strength					
(notched, 1/4 inch)	D256	kg · cm/cm	2	1	50
Specific gravity		—	1.02	1.19	1.19
Optical properties					
Refractive index		$n_D{}^{25}$	1.51	1.49	1.58
Total light transmission	D648	%	91	93	89
Haze	D648	%	2.1	1.8	2.3
Photoelastic coefficient	—[a]	10^8 MPa^{-1}	4	−6	90
Thermal properties					
Heat deflection temp.					
(18.6 kg/cm^2)	D1003	°C	166	81	137

[a] Ellipsometer was used.

The heat distortion temperature (HDT) of **poly-[1a + H$_2$]** is higher than the PC. It gave a colorless transparent material, which has a comparable total light transmission to other transparent resins. The UV-VIS spectrum of a 2.0-mm thick plate of **poly-[1a + H$_2$]** was maintained over a 90% transmittance through a 900 to 300 nm wave length. As expected from its nonpolar alicyclic structure, the photoelastic coefficient of **poly-[1a + H$_2$]** was comparable to PMMA and far smaller than PC. Low photoelastic coefficient is one of the most desirable properties for optical applications, especially for injection-molded optical parts. It should be noted that the specific gravity of **poly-[1a + H$_2$]** is about 20% smaller than that of PMMA and PC (1.02, 1.19, and 1.19, respectively). It is attributed to the bulky polycyclic structure of **poly-[1a + H$_2$]**. The fact that the specific gravity of the monomer **1a** is 1.06 indicates that there is no shrinkage but certain expansion through the polymerization and the following hydrogenation.

CONCLUSION

The ester group containing polycyclic monomers **1** underwent ring-opening polymerization in good yield and gave amorphous high T_g resins. The polymer with the cyano group (**poly-1g**) had too high a T_g to be determined by DSC. Some of the polymers were hydrogenated, resulting in greatly improved thermal stabilities. The degree of hydrogenation was an important factor for the improvement of the thermal stability. It was necessary to achieve as high a hydrogenation degree as possible to obtain a thermally stable polymer. The hydrogenated polymer **poly-[1a + H$_2$]** had good physical properties with excellent transparency.

REFERENCES

1. K. J. Ivin, *Olefin Metathesis,* Academic Press, New York, 1983.
2. V. Dragutan, A. T. Balaban, and M. Dimonie, *Olefin Metathesis and Ring-Opening Polymerization of Cyco-Olefins,* Wiley–Interscience, New York, 1985.
3. K. J. Ivin, J. J. Rooney, L. Bencze, J. G. Hamilton, L. M. Lam, G. Lapienis, B. S. R. Reddy, and H. T. Ho, *Pure Appl. Chem.,* **54,** 447 (1982).
4. F. W. Michelotti and W. P. Keaveney, *J. Polym. Sci., Part B,* **3,** 895 (1965).
5. R. E. Rinehart and H. P. Smith, *J. Polym. Sci., Part B,* **3,** 1049 (1965).
6. W. Ast, G. Rheinwald, and R. Kerber, *Makromol. Chem.,* **177,** 1349 (1976).
7. R. R. Schrock, *Acc. Chem. Res.,* **23,** 158 (1990).
8. M. Schimetta and F. Stelzer, *Macromolecules,* **27,** 3769 (1994).
9. M. G. Perrott and B. M. Novak, *Macromolecules,* **29,** 1817 (1996).
10. V. Heroguez, S. Breunig, Y. Gnanou, and M. Fontanille, *Macromolecules,* **29,** 4459 (1996).

11. S. Matsumoto, K. Komatsu, and K. Igarashi, *Am. Chem. Soc., Symp. Ser.,* **59,** 303 (1977).

12. S. Matsumoto, K. Komatsu, and K. Igarashi, *Am. Chem. Soc., Polym. Prepr.,* **18,** 110 (1977).

13. N. Calderon and R. L. Hinrichs, *Chem. Technol.,* 627 (1974).

14. W. Graulich, W. Swodenk, and D. Theisen, *Hydrocarbon Process.,* **51,** 71 (1972).

15. P. Guenther, F. Haas, G. Marwede, K. Nuetzel, W. Oberkirch, G. Pampus, W. Schoen, and J. Witte, *Angew. Makromol. Chem.,* **14,** 87 (1970).

16. R. Streck, *J. Mol. Catal.,* **15,** 3 (1982).

17. R. F. Ohm. *Chem. Technol.,* 183 (1980).

18. P. Le Delliou, *Caut. Plast.,* **77,** (1977).

19. J. Kodemura and T. Natsuume, *Polym. J.,* **27,** 1167 (1995).

20. B. H. Sohn, J. A. Gratt, J. K. Lee, and R. E. Cohen, *J. Appl. Polym. Sci.,* **58,** 1041 (1995).

21. The ^{1}H-NMR spectrum of the starting compound **1a** showed two sets of methoxy absorption in the same ratio (57/43).

22. K. J. Ivin, D. T. Laverty, and J. J. Rooney, *Makromol. Chem.,* **178,** 1545 (1977).

23. K. J. Ivin, G. Lapienis, and J. J. Rooney, *Polymer,* **21,** 436 (1980).

24. H. T. Ho, K. J. Ivin, and J. J. Rooney, *Makromol. Chem.,* **183,** 1629 (1982).

25. W. Abboud, A. Revillon, and A. Guyot, *New Polym. Mater.,* **1,** 155 (1989).

26. N. Seehof and W. Risse, *Macromolecules,* **26,** 5971 (1993).

27. F. C. Stehling and L. Mandelkern, *Macromolecules,* **3,** 242 (1970).

28. G. S. Trick, *J. Appl. Polym. Sci.,* **3,** 1253 (1960).

29. W. S. Bahary, D. I. Sapper, and J. H. Lane, *Rubber Chem. Technol.,* **40,** 1529 (1967).