Terpolymerization of Styrene, Norbornene, and Carbon Monoxide with a Palladium Catalyst

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ABSTRACT: In this work, the authors conducted the terpolymerization of carbon monoxide (CO), styrene (St), and norbornene (NBE) with $\text{Pd}(\text{CH}_3\text{COO})_2$ in CH_3OH under various molar ratios of norbornene to styrene at 90°C. Infrared spectra, ^1H NMR and ^{13}C NMR analyses confirmed that the NBE/St/CO terpolymers contain ketone, styrene unit, and ring structure of norbornene. Physical and thermal properties of the NBE/St/CO terpolymers were also investigated by a differential scanning calorimeter (DSC), thermogravimetric analysis (TGA), solubility and X-ray diffraction analyses. The results indicated that glass transition temperature (T_g) of the terpolymers increased when norbornene was introduced. Terpolymer increased molar ratio of norbornene to styrene was found to not only be more thermally stable, but also to increase solubility. As the NBE/St molar ratio became larger than 0.375 in terpolymer, the terpolymers were soluble in chloroform, tetrahydrofuran (THF), methylene chloride, ethyl acetate, benzene, dimethylacetamide (DMAc), and pyridine. X-ray diffraction results indicated that the terpolymer increased molar ratio of NBE/St in the terpolymer decreased the degree of crystallinity and the angle of maximum intensity owing to the bulky norbornene group. Hydrogenation of NBE/St/CO terpolymer with a reducing agent yielded a hydroxyl-containing polymer.

KEY WORDS Terpolymer / Polyketone / Carbon Monoxide / Norbornene / Styrene / Palladium Catalyst /

The polymerization of carbon monoxide (CO) and olefins is of increasing interest for the following reasons.¹ First, carbon monoxide is relatively inexpensive. Second, polymers containing polyketones have the potential to become photodegradable or biodegradable polymers in a new class.^{2–4} Third, because the carbonyl group can be easily modified chemically, polyketones are expected to be excellent starting materials in synthesizing functional polymers of a new type.^{5,6}

Although thoroughly discussing the terpolymerization of carbon monoxide, ethylene, and propylene, previous investigators have obtained only a few experimental results.^{8–10} Furthermore, the blending of the ethylene/propylene/CO terpolymer with other polymers (acrylonitrile–butadiene–styrene (ABS), polyarylsulfone)^{11,12} which subsequently enhance modulus and melt strength have also been studied. Although the terpolymerization of CO, styrene (St), with various olefins such as ethylene and propylene using palladium catalyst is patented,^{13–15} terpolymer involving CO, styrene, and norbornene (NBE) has received only slight attention. Other workers contend that the polymer containing norbornene groups has a thermoplastic nature.^{16,17} Other properties (e.g., glass fiber reinforcement, flame retardancy and impact toughness) have also been recognized.^{16,17} Thus, an approach to produce the new NBE/St/CO terpolymer having good thermal properties is of interest. Furthermore, the NBE/St/CO terpolymer can be hydrogenated to yield the hydroxyl-containing polymer which reacts with curing agents to obtain thermoset resins.¹⁸

This study presents results on the terpolymerization of CO, styrene and norbornene in the presence of $\text{Pd}(\text{CH}_3\text{COO})_2$ at 90°C. Measurements of IR spectra, ^1H NMR and ^{13}C NMR are also taken and analyzed. The influence of norbornene content in NBE/St/CO ter-

polymers on yield, molecular weight, thermal properties, solubility, and crystallinity are studied. Finally, the hydrogenation of the NBE/St/CO terpolymer with the reducing agent (lithium aluminum hydride, LiAlH_4) in tetrahydrofuran (THF) is also discussed.

EXPERIMENTAL

Materials

Carbon monoxide (99.3% purity) was purchased (Air Products and Chemicals Inc.). Norbornene (Merck) was distilled twice from calcium hydride under dry nitrogen (purity >99% by GC). Styrene (Merck) was dried over CaH_2 , distilled and stored under dry nitrogen in a refrigerator before used. Catalyst $\text{Pd}(\text{CH}_3\text{COO})_2$ and oxidant (1,4-naphthoquinone) were purchased from Merck, Germany. Ligand 2,2'-bipyridine (Merck) and *p*-toluenesulfonic acid (TCI) were used directly without purification. Solvents were purified according to standard methods.

Terpolymerization of Norbornene, Styrene, and Carbon Monoxide

To a solution containing $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.022 g, 0.1 mmol), 2,2'-bipyridine (0.47 g, 3 mmol), *p*-toluenesulfonic acid (0.34 g, 2 mmol), and 1,4-naphthoquinone (3.1 g, 20 mmol) in 30 ml CH_3OH were added styrene (48 ml, 0.4 mol) and norbornene (9.42 g, 0.1 mol). The mixture was placed in a 250 ml Parr bomb and charged with 2.8 MPa of CO under argon atmosphere. After stirring at 90°C for 2 h, a polymer precipitate (8.2 g) was obtained by adding methanol to the reaction mixture. The polymer product was washed with methanol and dried under vacuum. The polymer did not melt below 143°C. Osmometric measurements showed the NBE/St/CO terpolymer to have a number-average molecular weight ($\bar{M}_n$) ca. 3900.

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The above procedure was used in other reactions where the initial moles of norbornene were varied.

Measurements

TGA experiments were performed with a Perkin-Elmer thermal mechanical analyser Model TGS-II system. The glass-transition temperature (T_g) was measured with a Du Pont 9000 differential scanning calorimeter at a heating rate of $10^\circ\text{C min}^{-1}$. Molecular weight was determined by gel permeation chromatography (GPC). Four Waters (Ultrastaygel) columns 300×7.7 mm (10^2 , 10^3 , 10^4 , 10^5 in a series) were used for GPC analysis with THF (1 ml min^{-1}) as the eluent. The eluents were monitored with a UV detector (Gilson model 116) using a 254 nm. Polystyrene was used as the standard. Number-average molecular weight was determined by a vapor pressure osmometer (Knauer model 1100) in pyridine at 65°C . IR spectra were recorded using Bio-Rad FTS-40 (FTIR). ^1H and ^{13}C NMR (carbon frequency 100.40 MHz) spectra were recorded with a JEOL EX-400 spectrometer from $13 \text{ g}/100 \text{ cm}^3$ polymer solution in CDCl_3 at 30°C . Tetramethylsilane (TMS) was the internal standard. Partial resonance assignment was completed by Distortionless Enhancement following Polarization Transfer (DEPT) spectral acquisition procedures. An X-ray diffractometer was recorded using the powder method (Philips X-ray diffractometer, model PW 1710).

RESULTS AND DISCUSSION

Terpolymerization of CO with Styrene and NBE

The terpolymerization of styrene, norbornene, and carbon monoxide with catalyst palladium acetate in CH_3OH at 90°C was carried out. Table I summarizes the results at various molar ratios of norbornene to styrene. According to the table, increasing the molar ratio of norbornene to styrene resulted in enhanced of molecular weight and yield of the terpolymer. Number-average molecular weights ($\bar{M}_n$) of the terpolymers measured by GPC ranged from 3000–5000 and generally corresponded to those measured by VPO. This is consistent with the measured molar ratio of NBE/St from measurement of ^1H NMR spectra (see Table I) in terpolymers. That is, norbornene was found to be more reactive than styrene when copolymerized with carbon monoxide. Sen *et al.*^{19,20} has proposed that, in most olefins, the observed product that has reacted with carbon monoxide

is a vinyl ketone formed through a β -hydrogen abstraction step.^{19–21} However, in the case of norbornene, because of steric inaccessibility of the available β -hydrogen atoms, stable organometallic derivatives could be isolated.¹⁹ Thus, it could be easily polymerized with CO. Results obtained from the terpolymer structure are basis for as formula (1).

The infrared spectra of all the terpolymers in Table I include two features at 1725 and 1690 cm^{-1} that are attributed to carbonyl groups in ketones (repeating unit) and ester (end group), respectively. As described previously,^{7,22–24} the formation of polyketoester is considered to result from terpolymerization of the polymer end with CH_3OH as solvent.

Figure 1 shows TG thermograms of the terpolymers. Table II presents temperatures corresponding to initial

Figure 1. TGA curves of NBE/St/CO terpolymers in nitrogen (heating rate, $10^\circ\text{C min}^{-1}$): a) terpolymerization conditions: styrene (0.4 mol); CH_3OH (30 ml); $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.1 mmol); 2,2'-bipyridine (3 mmol); 1,4-naphthoquinone (20 mmol); *p*-toluenesulfonic acid (2 mmol); temperature, 90°C ; partial pressure of CO, $P(\text{CO}) = 2.8 \text{ MPa}$; reaction period, 2 h. b) TP-1, —; TP-2, —; TP-3, —; TP-4, —; TP-5, —; TP-6, —.

Table I. Terpolymerization of CO with styrene and norbornene^a

Polymer code	NBE/St molar ratio	Yield	Productivity	$\bar{M}_n^b$ (GPC)	$\bar{M}_n^c$ (VPO)	$\nu_{\text{C=O}}$ cm^{-1}	NBE/St molar ratio ^d
		g	g polymer $\text{g}^{-1} \text{ Pd h}^{-1}$				
TP-1	0	6.25	294	—	—	1750, 1698	— ^e
TP-2	0.25	8.17	384	2960	3900	1725, 1690	— ^e
TP-3	0.375	10.36	487	3320	4400	1725, 1690	0.57
TP-4	0.50	15.63	735	4040	4600	1725, 1690	1.41
TP-5	0.75	18.44	867	4430	4800	1725, 1690	2.16
TP-6	1.00	20.70	973	4770	4900	1725, 1690	2.80

^a Experimental conditions: styrene (0.4 mol); CH_3OH (30 ml); $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.1 mmol); 2,2'-bipyridine (3 mmol); 1,4-naphthoquinone (20 mmol); *p*-toluenesulfonic acid (2 mmol); temperature, 90°C ; partial pressure of CO, $P(\text{CO}) = 2.8 \text{ MPa}$; reaction period, 2 h. ^b Number-average molecular weight determined by GPC (polystyrene standards). ^c Number-average molecular weight determined by VPO in pyridine at 65°C . ^d Molar ratio of NBE/St was calculated from ^1H NMR spectra; CDCl_3 was used as solvent. ^e Polymer was insoluble in CDCl_3 .

Table II. Thermal properties of the terpolymer^a

Polymer code	NBE/St molar ratio	T_g^b	T_d^{ic}	$T_d^{50\%d}$	T_d^{maxe}	Char yield at 500°C %
		°C	°C	°C	°C	
TP-1	0	67	306	363	366	5
TP-2	0.25	90	326	371	368	17
TP-3	0.375	102	327	401	398	26
TP-4	0.50	116	328	411	409	26
TP-5	0.75	120	329	426	423	26
TP-6	1.00	143	377	433	430	26

^a Experimental conditions: styrene (0.4 mol); CH₃OH (30 ml); Pd(CH₃COO)₂ (0.1 mmol); 2,2'-bipyridine (3 mmol); 1,4-naphthoquinone (20 mmol); *p*-toluenesulfonic acid (2 mmol); temperature, 90°C; partial pressure of CO, P(CO)=2.8 MPa; reaction period, 2 h. ^b DSC analysis conducted at a heating rate of 10°C min⁻¹. ^c Thermogravimetric analysis conducted at a heating rate of 10°C min⁻¹ in nitrogen. ^d $T_d^{50\%}$ is the temperature at which 50% loss of mass was observed. ^e T_d^{max} is the temperature at which maximal loss of mass was observed.

mass loss (T_d^i), 50% mass loss ($T_d^{50\%}$), inception of fast degradation (T_d^{max}) and char yield remaining at 500°C. All the polymers remains stable up to 300°C and start degrading between 306°C and 377°C. The experimental results indicate that increasing the molar ratio of norbornene to styrene is more thermally stable than St/CO copolymer. That is, polymer chains with more ring structures of norbornene should provide a greater thermal stability. As the concentration of norbornene increases, T_g also increases due to the bulkiness of the ring structure unit of norbornene which hinders polymer chain movement.

X-Ray Diffractogram of Terpolymer

X-Ray diffractograms of various terpolymers appear in Figure 2 as intensity vs. 2θ , where θ is the angle of diffraction (Bragg angle). Table III presents the crystallinities of various terpolymers. From Figure 2 and Table III, the degree of crystallinity decreases with increase in the molar ratio of norbornene to styrene. A previous work²⁵ indicated that the St/CO copolymer has a syndiotactic structure. However, under the same experimental conditions, with increasing norbornene content, the styrene/CO units became increasingly isolated, thereby resulting in loss of tactic styrene/CO blocks and, ultimately, decreased crystallinity of terpolymer.²⁶ The angle of maximum intensity of X-ray diffraction of terpolymers was altered from 23.9° to 17.6°.

This may be accounted for by the bulky norbornene group, which increases the distance between polymer chains.^{27,28}

The solubility of the terpolymer depends on the molar ratio of norbornene to styrene in the terpolymers. For instance, the copolymer of carbon monoxide with styrene is insoluble in common organic solvents such as chloroform, THF, and methylene chloride.²⁶ Terpolymers introducing a norbornene content larger than 0.375 molar ratio to styrene would cause them to be soluble in chloroform, THF, methylene chloride, ethyl acetate, benzene, dimethylacetamide, and pyridine. Solubility generally increases with decreasing crystallinity.²⁹

Characterization of NBE/St/CO Terpolymer by IR, ¹H NMR, and ¹³C NMR

The terpolymer of NBE, styrene, and CO was characterized by IR, ¹H NMR, and ¹³C NMR spectroscopy. Strong IR absorption about 1690 cm⁻¹ is ascribed to

Figure 2. X-Ray diffractograms of NBE/St/CO terpolymers: Terpolymerization conditions: styrene (0.4 mol); CH₃OH (30 ml); Pd(CH₃COO)₂ (0.1 mmol); 2,2'-bipyridine (3 mmol); 1,4-naphthoquinone (20 mmol); *p*-toluenesulfonic acid (2 mmol); temperature, 90°C; partial pressure of CO, P(CO)=2.8 MPa; reaction period, 2 h.

Table III. Crystallinity of the terpolymer^a

Polymer code	NBE/St molar ratio	Crystallinity
		%
TP-1	0	50.1
TP-2	0.25	45.5
TP-3	0.375	39.2
TP-4	0.50	38.8
TP-5	0.75	37.0
TP-6	1.00	36.7

^a Experimental conditions: styrene (0.4 mol); CH₃OH (30 ml); Pd(CH₃COO)₂ (0.1 mmol); 2,2'-bipyridine (3 mmol); 1,4-naphthoquinone (20 mmol); *p*-toluenesulfonic acid (2 mmol); temperature, 90°C; partial pressure of CO, P(CO)=2.8 MPa; reaction period, 2 h.

the carbonyl group (Table I, TP-4). The absorption at 1294 cm^{-1} indicates an intact methylene bridge of the NBE group. Absorptions at $3100\text{--}3000\text{ cm}^{-1}$ and $3000\text{--}2800\text{ cm}^{-1}$ are ascribed to aromatic C–H stretching and aliphatic C–H stretching of the styrene and norbornene groups, respectively. Aliphatic C–H deformation and aromatic C–C stretching absorption are located at $1500\text{--}1430\text{ cm}^{-1}$. Absorptions at 870, 750, and 700 cm^{-1} are ascribed to aromatic C–H deformation. According to Figure 3, the ^1H NMR spectrum (CDCl_3) of the terpolymer shows broad absorption at 0.6–3.8 ppm. Absorption at 0.60–3.8 ppm is to the ring structure of norbornene^{23,30} overlapping with the styrene group. Absorption at 6.55–7.15 ppm is due to the styrene group. The alternating St/CO copolymer prepared according to ref 25 was syndiotactic, and thus with increasing norbornene content, the styrene/CO units became increasingly isolated, thereby resulting in loss of the tactic styrene/CO blocks. Ultimately, a broad ^1H NMR spec-

Figure 3. ^1H NMR spectrum of NBE/St/CO terpolymer: Solvent, CDCl_3 . Terpolymerization conditions: styrene (0.4 mol); norbornene (0.2 mol); CH_3OH (30 ml); $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.1 mol); 2,2'-bipyridine (3 mmol); 1,4-naphthoquinone (20 mmol); *p*-toluenesulfonic acid (2 mmol); temperature, 90°C ; partial pressure of CO, $P(\text{CO})=2.8\text{ MPa}$; reaction period, 2 h.

Figure 4. ^{13}C NMR and DEPT spectra of the NBE/St/CO terpolymer. Solvent, CDCl_3 . Terpolymerization conditions: styrene (0.4 mol); norbornene (0.2 mol); CH_3OH (30 ml); $\text{Pd}(\text{CH}_3\text{COO})_2$ (0.1 mmol); 2,2'-bipyridine (3 mmol); 1,4-naphthoquinone (20 mmol); *p*-toluenesulfonic acid (2 mmol); temperature, 90°C ; partial pressure of CO, $P(\text{CO})=2.8\text{ MPa}$; reaction period, 2 h.

trum was obtained.²⁶

Figure 4 shows the ^{13}C NMR spectrum of the NBE/St/CO terpolymer. The signal at 208 ppm is attributed to the carbonyl carbon. The line at 173 ppm is due to the ester group ($\text{CH}_3\text{--O--(C=O)--}$) at the end of the terpolymer chain. In this figure, the peaks in the DEPT (distortionless enhancement by polarization transfer) spectrum are also shown. Signals at 20–55 ppm support that the terpolymer contains ring structures. Signals around 28 ppm, as expected for the C-5 and C-6 of *exo*-substituted bicycloheptanes, are present. Signals appearing at higher field *ca.* 22 ppm which correspond to *endo* carbons are also present.³¹ Their presence implies that norbornene-CO sequences not only have *cis, exo* stereochemistry, but also *endo* stereochemistry.^{31–35} Signals appearing at 145, 126, 125.5, 123.5, 53.3, and 42.3 ppm are due to styrene groups. This further confirms that CO is definitely polymerized with norbornene and styrene.

Hydrogenation

Because the carbonyl group can be easily modified chemically, polyketones are expected to be excellent starting materials for synthesizing functional polymers which react with curing agents to yield thermoset resins. Hydrogenation of polyketones with a reduction agent (lithium aluminum hydride, LiAlH_4) in THF at 65°C yielded hydroxyl-containing polymer represented as in (eq 2) and Figure 5. The hydrogenated polymer was

completely soluble in chloroform, methylene chloride, ethyl acetate, THF, dimethylacetamide, pyridine, and benzene, and partially soluble in dimethylsulfoxide,

Figure 5. IR spectra of hydrogenated polyketones with a reducing agent (lithium aluminum hydride, LiAlH_4) in THF at 65°C . (a) before; (b) after hydrogenation.

acetone, and insoluble in *n*-hexane and methanol. The absence of infrared absorption corresponding to the carbonyl group [1694 cm^{-1} , Figure 5(a)] and specific absorption of ν_{OH} at 3430 cm^{-1} [Figure 5(b)] indicate the essentially complete conversion of ketone functional groups to alcohol groups without cleavage of the polyketone chain. According to the ^{13}C NMR spectrum, the appearance of the signal due to the methine group at 68 ppm and disappearance of the signal due to the carbonyl group at 208 ppm after hydrogenation confirm the complete hydrogenation of the polyketone.

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REFERENCES

1. A. Sen, *Adv. Polym. Sci.*, **73/74**, 125 (1986).
2. M. Heskin and J. E. Guillet, *Macromolecules*, **3**, 224 (1970).
3. G. H. Hartley and J. E. Guillet, *Macromolecules*, **1**, 413 (1968).
4. G. H. Hartley and J. E. Guillet, *Macromolecules*, **1**, 165 (1968).
5. M. M. Brubaker, D. D. Coffman, and H. H. Hoehn, *J. Am. Chem. Soc.*, **74**, 1509 (1952).
6. Y. Morishima, T. Tadizawa, and S. Murahashi, *Eur. Polym. J.*, **9**, 669 (1973).
7. E. Drent, J. A. M. Van Broekhoven, and M. J. Doyle, *J. Organomet. Chem.*, **417**, 235 (1991).
8. E. Drent, Eur. Patent, Appl. EP 229408 (1987).
9. J. Van Broekhoven, Eur. Patent Appl. EP 361584 (1989).
10. P. K. Wong, J. J. Reijssper, and A. W. Vander Made, Eur. Patent Appl. EP 408155 (1990).
11. W. P. Gergen, U.S. Patent 4900789 (1990).
12. W. P. Gergen and R. G. Lutz, U.S. Patent 4904744 (1990).
13. E. Drent and R. L. Wife, U.S. Patent 4970294 (1990).
14. P. K. Wong, Eur. Patent Appl. EP 384517 (1990).
15. P. K. Wong, Eur. Patent Appl. EP 404228 (1990).
16. R. Strenk, "Olefin Metathesis and Polymerization Catalysts," Y. Imamoglu, B. Z. Karan, and A. J. Amass, Ed., Kluwer, The Netherlands, 1990, p 472.
17. Anon, *Plastic Focus*, **14**, 3 (1982).
18. A. A. Smaardijk and A. H. Kramer, Eur. Patent Appl. EP. 372602 (1989).
19. A. Sen, *Acc. Chem. Res.*, **26**, 303 (1993).
20. J. S. Brumhaugh, R. R. Whittle, M. A. Parvez, and A. Sen, *Organometallics*, **9**, 1735 (1990).
21. F. Ozawa, T. Hayashi, H. Koide, and A. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1469 (1991).
22. D. J. Liaw, *J. Polym. Sci., Polym. Chem. Ed.*, **31**, 309 (1993).
23. D. J. Liaw and B. F. Lay, *Polym. J.*, **28**, 266 (1996).
24. T. W. Lai and A. Sen, *Organometallics*, **3**, 866 (1984).
25. B. Vincezo, C. Paoio, L. Laura, and M. Trifuoggi, *Makromol. Chem., Rapid Commun.*, **14**, 261 (1993).
26. A. Sen and Z. Jiang, *Macromolecules*, **26**, 911 (1993).
27. D. J. Liaw and S. P. Lin, *J. Appl. Polym. Sci.*, in press.
28. D. J. Liaw and S. P. Lin, *Eur. Polym. J.*, in press.
29. D. J. Liaw, *J. Polym. Sci., Polym. Chem. Ed.*, **33**, 605 (1995).
30. F. Hojabri, M. M. Mohaddes and A. Talab, *Polymer*, **17**, 710 (1976).
31. D. Roberto, M. Catellani, and G. P. Chiusoli, *Tetrahedron Lett.*, **29**, 2115 (1988).
32. J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N.Y., 1972, p 178.
33. D. E. James and J. K. Stille, *J. Org. Chem.*, **41**, 1504 (1976).
34. E. Lippmaa, T. Pehk, N. A. Belikova, A. A. Bobyleva, A. N. Bobyleva, A. N. Kalinichenko, M. D. Ordubadi, and A. F. Plate, *Org. Magn. Res.*, **8**, 74 (1976).
35. K. Laihia, J. Paasvirta, H. Pikkarainen, and S. Aho-Pullinen, *Org. Magn. Res.*, **72**, 117 (1984).