Macromolecules **2003,** *36,* 2573−2575

Communications to the Editor

Topochemical Polymerization of N-Substituted Sorbamides To Provide Thermally Stable and Crystalline Polymers

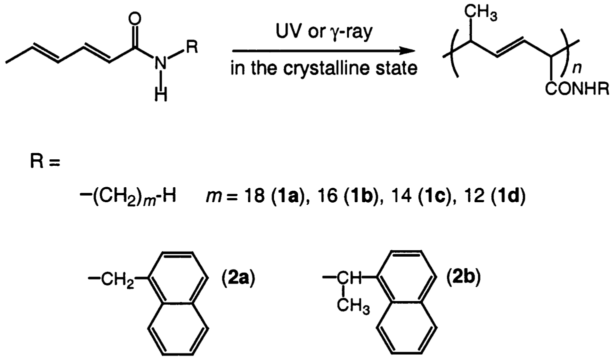
Akikazu Matsumoto,*,†,‡ Tsuyoshi Chiba,† and Kunio Oka§

Department of Applied Chemistry, Graduate School of Engineering, Osaka City University and PRESTO, Japan Science and Technology Corporation (JST), Conversion and Control by Advanced Chemistry, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan, and Research Institute for Advanced Science and Technology, Osaka Prefecture University, Gakuencho 1-2, Sakai, Osaka 599-8570, Japan

Received July 22, 2002
Revised Manuscript Received January 22, 2003

Introduction. Crystal engineering is the designing of structures and properties of crystalline materials using preorganized molecules through intermolecular interactions such as coordination, hydrogen bonds, $\pi\cdots\pi$, CH/π, and halogen or sulfur atom interactions.[1] We have recently revealed the features and mechanisms of the topochemical polymerization of 1,3-diene monomers including some ester and ammonium derivatives of the muconic and sorbic acids, which are 1,3-diene di- and monocarboxylic acid derivatives, respectively.[2] These monomers provide stereoregular polymers under UV, X-ray, and γ-ray irradiation in the crystalline state when a well-designed substituent is introduced into the ester and N-substituted groups. For example, the ethyl, 4-chloro-, and 4-bromobenzyl esters of (*Z*,*Z*)-muconic acid topochemically polymerize, while the other ester derivatives isomerize to the corresponding *E*,*E* isomers or have no reactions.[3] In the series of alkylammonium derivatives of (*Z*,*Z*)-muconic acid, the introduction of benzyl, naphthylmethyl, and long-alkyl (higher than decyl) groups as the N substituents in the ammonium group effectively induces the polymerization.[4] Especially, the naphthylmethylammonium substitution is the most suitable for the design of a monomer crystal structure because it is superior as the supramolecular synthon[5] for monomer stacking during the topochemical polymerization of 1,3-diene monomers such as (*Z*,*Z*)-muconic acid as well as the (*E*,*E*)-muconic and sorbic acid derivatives.[6] A naphthylmethylammonium group can arrange diene monomer molecules with the stacking distance of 4.9 Å in the crystals. This distance is constructed by the two-dimensional hydrogen bond network, aromatic stacking with a herringbone structure, and CH/π interactions in the crystals.[7] The strategy using a naphthylmethyl group as the supramolecular synthon was also valid for various kinds of diene monomers other than the muconic and sorbic acid derivatives.

Scheme 1



In contrast to the results of the successful polymerization of the ammonium and ester derivatives, no polymerization has been reported for the amide derivative of the 1,3-diene carboxylic acids, except for *N*-octadecylsorbamide.[8] In the 1980s, the solid-state polymerization of 1,3-diene compounds was reported for some 6-amino-2,4-hexadienenoic derivatives with a layered structure, resulting in the formation of stereoregular polymers.[9] Tieke also referred to the γ-radiation polymerization of *N*-octadecylsorbamide.[8] However, the polymerization mechanism and crystal structure of the amide derivative as well as the characterization of the resulting polymer are still undetermined over the past two decades. Recently, we have confirmed that the topochemical polymerization proceeds under UV- and γ-radiation in the crystalline state when naphthylmethyl and higher *n*-alkyl groups are introduced as the N substituent of the amide derivatives, as expected (Scheme 1). In this paper, we describe the polymerization behavior of the N-substituted sorbamides and some properties of the obtained polymers. The resulting polymers have thermal stability superior to the corresponding ammonium derivatives previously reported.

Results and Discussion. Table 1 summarizes the results of the UV- and γ-irradiation polymerization of several N-substituted sorbamides. The polymerization proceeded in the absence of air or oxygen under UV- and γ-irradiation to give polymers in a high yield when the naphthylmethyl and *n*-alkyl groups with a carbon number greater than 10 were introduced as the N substituents. The *N*-alkyl derivatives with a shorter *n*-alkyl group having a carbon number less than 8 provided no polymer under identical conditions, similar to the polymerization reactivity of the *n*-alkylammonium (*Z*,*Z*)-muconates.[4c] During the polymerization of these monomers, the atmospheric conditions are important for determining the polymerization reactivity and the resulting products. The photoirradiation in the presence of oxygen provided a soluble oligomer, which is an alternating copolymer of the sorbamides and

---

† Osaka City University.
‡ PRESTO-JST.
§ Osaka Prefecture University.
* Corresponding author: FAX +81-6-6605-2981; e-mail matsumoto@a-chem.eng.osaka-cu.ac.jp.

10.1021/ma021167a CCC: $25.00

Table 1. UV- and γ-Irradiation Polymerization of N-Substituted Sorbamide Derivatives in the Absence of Oxygen under Various Conditions

UV-irradiation[a]				γ-irradiation[b]		
monomer	temp (°C)	time (h)	yield (%)	monomer	dose (kGy)	yield (%)
1a	r.t.	75	36	**1a**	10	30
	60	30	24		100	74
	80	10	33		200	93
	80	20	40	**1b**	200	90
	80	30	51	**1c**	200	87
2a	60	30	54	**1d**	10	20
	80	10	51		100	91
	80	20	70		200	97
	80	30	82	**2a**	200	85
2b	80	30	5	**2b**	200	7

[a] In a degassed Pyrex tube under UV-irradiation with a high-pressure Hg lamp (100W) at a distance of 10 cm. [b] In a degassed Pyrex tube under γ-irradiation at a dose rate of 48.5 kGy/h at room temperature.

oxygen with a molecular weight of 10^3. Similar peroxide polymer formation has already been reported for the photoreactions and thermal reactions of the sorbic esters as well as many kinds of vinyl monomers with oxygen.[10,11]

The polymer yield increased as the UV-irradiation time, the γ-ray radiation dose, and the polymerization temperature increased (Table 1), but the reactivity was independent of the length of the *N*-alkyl group (**1a**−**1d**) under these conditions due to the expected structure for similar monomer stacking in the crystals. The polymerization reactivity of these amide derivatives is lower than those of the ester and ammonium derivatives of the muconic and sorbic acids with similar substituents.[2] The naphthylmethyl group as the N-substituent (**2a**) resulted in a high polymer yield,[12] whereas the presence of the α-methyl group (**2b**) drastically decreased the polymerization reactivity.

All the polymers obtained from the sorbamides in this work were insoluble. Unreacted monomers were recovered from a soluble part by extraction with chloroform, and any other product was not detected. IR spectroscopy confirmed the *trans*-2,5-structure as the repeating units of the polymers irrespective of the structure of the N substituents and the polymerization conditions (light source and temperature). It has been reported that different reaction modes were induced by the different activated species depending on the type of radiation of the same 1,3-diene compounds.[14] Namely, UV- and γ-radiation resulted in the formation of different products, cyclodimers and polymers. In our series of muconic or sorbic esters, amides, and ammoniums, however, a single product has been obtained from one monomer independent of the radiation conditions unless polymorphs are present.

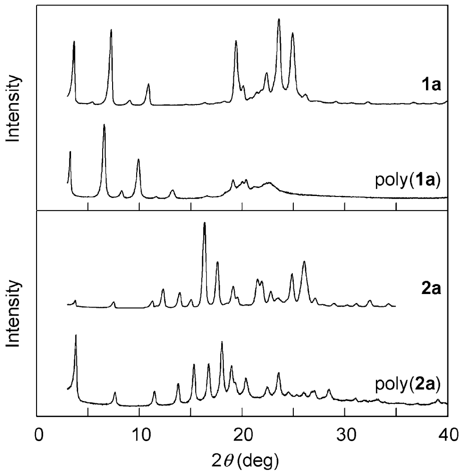


Figure 1. Powder X-ray diffraction profiles of N-substituted sorbamide monomers and the polymers obtained by γ-irradiation polymerization with a dose of 200 kGy in the crystalline state.

Table 2. 2θ Values of Low-Angle Peak in X-ray Diffraction and Calculated Interlayer Distance (*d*) for the Crystals of N-Substituted Sorbamides and Their Polymers[a]

monomer	2θ (deg)	*d*(interlayer) (Å)	polymer	2θ (deg)	*d*(interlayer) (Å)
1a	3.64[f]	48.5	poly(**1a**)	3.28[f]	53.9
1b	3.88[f]	45.5	poly(**1b**)	3.60[f]	49.1
1c	4.32[f]	40.9	poly(**1c**)	3.88[f]	45.5
1d	4.74[f]	37.3	poly(**1d**)	4.34[f]	40.7
2a	3.76[f]	47.0	poly(**2a**)	3.82[f]	46.2
3[b]	1.93	45.8	poly(**3**)	2.02	43.7
4[c]	4.00	23.0	poly(**4**)	4.11	21.5
5[d]	3.97	22.3	poly(**5**)	4.05	21.8
6[e]	3.19[f]	55.4	poly(**6**)	3.21[f]	55.0

[a] Determined by powder X-ray diffraction (Cu Kα, $\lambda = 1.541\ 78$ Å). [b] Di(octadecylammonium) (*Z*,*Z*)-muconate (ref 4c). [c] Di(1-naphthylmethylammonium) (*Z*,*Z*)-muconate (ref 4b). [d] Di(1-naphthylmethylammonium) (*E*,*E*)-muconate (ref 4b). [e] 1-Naphthylmethylammonium sorbate (ref 6). [f] Assigned as the 200 plane.

Powder X-ray diffraction has revealed the crystal-to-crystal process of polymerization (Figure 1). A diffraction peak observed at a lower angle region indicates that these monomer crystals have a layered structure with a thickness of 37.3−48.5 and 47.0 Å for **1a**−**1d** and **2a**, respectively. Each stacking distance was maintained during the polymerization and observed after the γ- or UV-irradiation (Table 2). Similar *d*(interlayer) values are observed for the layered structure of the *n*-alkyl- and naphthylmethylammonium muconates and sorbates (**3**−**6** in Table 2).[2,4] In contrast, the diffraction peaks of the **2b** crystal changed and broadened during the photoirradiation (see Supporting Information). It suggests the collapse of the crystal structure during the initial stage of the polymerization, resulting in a very low polymer yield.

Preliminary X-ray single-crystal structure analysis of the amide derivatives[15] suggests the monomer stacking in a sheet by the formation of a linear hydrogen bond chain between the C═O and N−H groups (Figure 2). The intermolecular hydrogen bond (*d*(HB)) of the amide as the supramolecular synthons consists of a 5 Å repeating unit.[16] This value is appropriate for the topochemical polymerization of 1,3-dienes,[7] but the direction of the diene moieties (overlap of π-orbital) is not suited for the reaction along the direction of the amide hydrogen bonds. Probably, polymerization would occur when the stacking phase between the molecular sheets satisfies the polymerization principles, i.e., the stacking distance of the monomers in the intersheet direction (*d*(intersheet)) is approximately equal to 5 Å.

Poly(**1**)s and poly(**2a**) are thermally stable, and the onset temperatures of their decompositions (T_{init}) were 315 and 342 °C, respectively, being much higher than those of the polymers from the *N*-benzyl- and *N*-naphthylmethylammonium muconates and sorbates.[17] These crystalline polymers have no clear melting point below the T_{init}, but poly(**1a**) was found to show any transition possibly related to side-chain crystallization

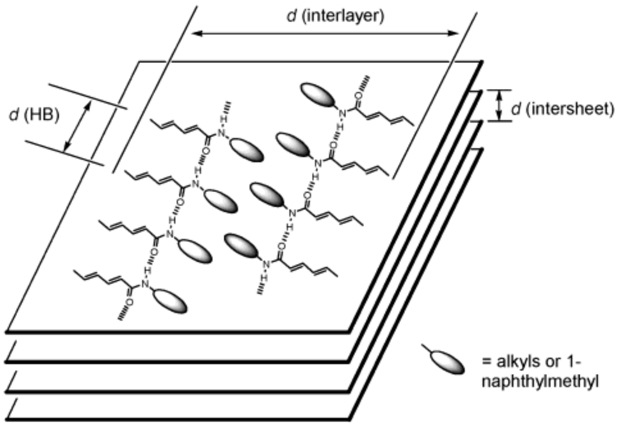


Figure 2. Proposed stacking model of N-substituted sorbamides in the crystals. *d*(interlayer) is the interlayer distance of the lamella crystals consisting of diene and N-substituent layers. *d*(HB) is the monomer stacking distance along the hydrogen bond chains connecting the C=O and N−H groups in a sheet. *d*(intersheet) is the stacking distance between the monomer layers.

in the temperature range 100−150 °C. An intermolecular hydrogen bond is expected to reinforce the polymer chain aggregation in the solids, resulting in tough and strong polymer materials similar to polyamides obtained by condensation polymerization. We are now further investigating their polymer structure and properties as well as single-crystal structure analysis for polymerizable and nonpolymerizable monomer crystals.

Acknowledgment. This work was financially supported by JST and by a Grant-in-Aid for Scientific Research (B) (No. 13450381) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

Supporting Information Available: Experimental procedures, IR spectra, powder X-ray diffraction, and thermogravimetric curves. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids;* Elsevier: Amsterdam, 1989. (b) *Comprehensive Supramolecular Chemistry*; MacNicol, D. D., Toda, F., Bishop, R., Eds.; Pergamon: Oxford, 1996; Vol. 6. (c) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999.

(2) (a) Matsumoto, A.; Odani, T. *Macromol. Rapid Commun.* **2001**, *22*, 1195−1215. (b) Matsumoto, A. *Polym. J.* **2003**, *35*, 93−121.

(3) (a) Matsumoto, A.; Yokoi, K.; Aoki, S.; Tashiro, K.; Kamae, T.; Kobayashi, M. *Macromolecules* **1998**, *31*, 2129−2136. (b) Matsumoto, A.; Katayama, K.; Odani, T.; Oka, K.; Tashiro, K.; Saragai, S.; Nakamoto, S. *Macromolecules* **2000**, *33*, 7786−7792. (c) Matsumoto, A.; Tanaka, T.; Tsubouchi, T.; Tashiro, K.; Saragai, S.; Nakamoto, S. *J. Am. Chem. Soc.* **2002**, *124*, 8891−8902.

(4) (a) Matsumoto, A.; Odani, T.; Chikada, M.; Sada, K.; Miyata, M. *J. Am. Chem. Soc.* **1999**, *121*, 11122−11129. (b) Odani, T.; Matsumoto, A. *Macromol. Rapid Commun.* **2000**, *21*, 41−44. (c) Matsumoto, A.; Odani, T.; Sada, K.; Miyata, M.; Tashiro, K. *Nature (London)* **2000**, *405*, 328−330.

(5) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311−2327.

(6) Matsumoto, A.; Nagahama, S.; Odani, T. *J. Am. Chem. Soc.* **2000**, *122*, 9109−9119.

(7) Matsumoto, A.; Sada, K.; Tashiro, K.; Miyata, M.; Tsubouchi, T.; Tanaka, T.; Odani, T.; Nagahama, S. Tanaka, T.; Inoue, K.; Saragai, S.; Nakamoto, S. *Angew. Chem., Int. Ed.* **2002**, *14*, 2502−2505.

(8) Tieke, B. *Colloid Polym. Sci.* **1985**, *263*, 965−972.

(9) (a) Tieke, B.; Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 687. (b) Tieke, B. *Adv. Polym. Sci.* **1985**, *71*, 79−151. (c) Tieke, B. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 391−406. (d) Tieke, B.; Chapuis, G. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2895−2921. (e) Tieke, B.; Chapuis, G. *Crystallographically Ordered Polymers*; Sandman, D. J., Ed.; ACS Symposium Series Vol. 337; Washington, DC, 1987; pp 61−78. (f) Tieke, B. Chapuis, G. *Mol. Cryst. Liq. Cryst.* **1986**, *137*, 101−116.

(10) (a) Matsumoto, A.; Ishizu, Y.; Yokoi, K. *Macromol. Chem. Phys.* **1998**, *199*, 2511−2516. (b) Matsumoto, A.; Higashi, H. *Macromolecules* **2000**, *33*, 1651−1655.

(11) (a) Bhanu, V. A.; Kishore, K. *Chem. Rev.* **1991**, *91*, 99−117. (b) Mukundan, T.; Kishore, K. *Prog. Polym. Sci.*. **1990**, *15*, 475−505.

(12) In our earlier work (ref 13), we reported no polymerization of **2a** under UV-irradiation at room temperature for 8 h, contrary to the results in this study. It is due to the polymorphs. We succeeded in the single-crystal growth and determination by the X-ray crystal structure analysis for **2a**. The obtained crystal was inert to photoirradiation, and its structure was different form that of powdery crystals polymerized in this study.

(13) Matsumoto, A.; Odani, T. *Polym. J.* **1999**, *31*, 717−719.

(14) Augenstein, M.; Wegner, G. *Makromol. Chem.* **1988**, *189*, 163−184.

(15) We have examined the photoreactivity and single-crystal structures for a large number of *N*-phenyl- and *N*-benzylsorbamides with various substituents on the aromatic ring. However, we have yet not found polymerizable crystals of the *N*-phenyl and *N*-benzyl derivatives.

(16) (a) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120−126. (b) Aakeröy, C. B.; Seddon, K. R. *Chem. Soc. Rev.* **1993**, *22*, 397−407. (c) MacDonald, J. C.; Whitesides, G. M. *Chem. Rev.* **1994**, *94*, 2383−2420. (d) Meléndez, R. E.; Hamilton, A. D. *Top. Cur. Chem.* **1998**, *198*, 97−129.

(17) Nagahama, S.; Matsumoto, A. *J. Am. Chem. Soc.* **2001**, *123*, 12176−12181.

MA021167A