Man-made urushi

Preparation of crosslinked polymeric films from renewable resources via air-oxidation processes

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(Communicated by Seizo OKAMURA, M. J. A., Dec. 12, 2000)

Abstract: "Man-made (artificial) urushi" has been prepared by laccase-catalyzed curing of new urushiol analogues, which were facilely synthesized by lipase-catalyzed regioselective acylation of catechol derivatives having a primary alcohol with unsaturated fatty acids derived from plant oils, one of the most important renewable resources. The curing of the catechol derivative having two or three unsaturated group proceeded under mild reaction conditions to produce the crosslinked film ("man-made urushi") with high hardness and gloss surface, which are comparable with those of natural urushi coating. Similar urushiol analogues from 4-hydroxyphenetyl alcohol and unsaturated fatty acids were subjected to an oxidative polymerization by Fe-salen catalyst, yielding soluble polyphenols having the unsaturated group in the side chain. Cardanol, a phenol derivative mainly having a C15 unsaturated hydrocarbon chain with 1-3 double bonds at m-position, is obtained from cashew nut shell liquid. Oxidative polymerization of cardanol by peroxidase or Fe-salen catalyst gave the crosslinkable polyphenol. These prepolymers were subjected to hardening by thermal treatment or cobalt naphthenate catalyst to give a crosslinked film (also, "man-made urushi") with good hardness.

Key words: Man-made urushi; urushiol analogue; laccase; curing; renewable resource; oxidative polymerization.

Introduction. Urushi is a typical Japanese traditional coating. It shows excellent toughness and brilliance for a long period, and thus, caused much interest for organic chemists. Urushi coating is prepared from sap of Japanese lacquer tree (*Rhus vernicifera*),[1)–3)] and Majima's pioneering work in the early days of this century revealed that main important components of urushi are "urushiols", whose structure is a catechol derivative with unsaturated hydrocarbon chains consisting of a mixture of monoenes, dienes, and trienes at 3- or 4-position of catechol.[4)–6)] Typical urushiols are shown in Chart 1. Crosslinking of the urushiol is supposed to be accomplished mainly by a laccase-catalyzed oxidative coupling of the phenol moiety of the urushiol and a subsequent oxidation of unsaturated alkyl chains in air.[7),8)]

Usushi can be regarded as the only example of practical natural paints utilizing *in vitro* enzymatic catalysis for hardening. The film-forming from the urushiol proceeds under air at room temperature without organic solvents, and hence, urushi seems very desirable for coating materials from the environmental standpoint. However, modeling study of urushi has been limited for only one paper.[9)] This is mainly due to the difficulty in preparation of the urushiol.

Polymerizations catalyzed by enzymes (enzymatic polymerizations) have received much attention as new methodology of polymer syntheses.[10)–15)] Characteristics of enzyme catalysis are expected to provide new polymeric materials, which are difficult to be obtained by conventional methods. Peroxidases induced the oxidative polymerization of phenol derivatives under mild reaction conditions to produce a new class of functional

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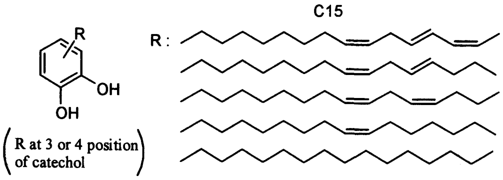
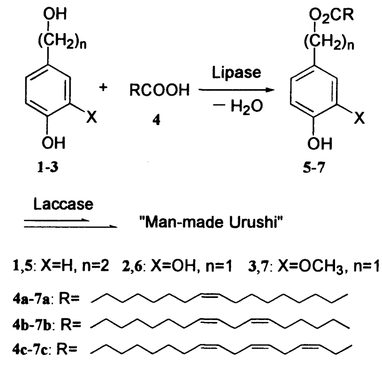


Chart 1

polyphenols in good yields. This process does not use toxic formaldehyde and their synthetic procedure is very facile. In the peroxidase-catalyzed polymerization of phenol derivatives having an unsaturated group, the phenolic moiety was chemoselectively polymerized to give new reactive polymers, which were subjected to thermal and photochemical curings.[16),17)]

Potential demands for replacing petroleum-derived raw materials with renewable plant-based ones in production of polymeric materials are quite world-widely significant in the social and environmental viewpoints.[18)] Using such plant-based raw materials contributes to global sustainability without depletion of scarce important resources. Furthermore, these materials are often cheaper than petrochemicals. The present article describes our recent progress on preparation of man-made (artificial) urushi,*) new crosslinked polymeric films, from urushiol analogues (phenols having an unsaturated group in the side chain).[19)–25)] All the monomers are derived from plant oils. In the curing stage, the crosslinked polymeric film can be obtained in the absence of organic solvents at an ambient temperature under air. Therefore, our new methodology can be regarded as an environmentally benign process of polymer coating, providing an example system of *green polymer chemistry*.[26)]

Results and discussion. *Laccase-catalyzed hardening of urushiol analogues.*[19)–20)] We designed new urushiol analogues (**5**~**7**), in which the unsaturated group is connected with the catechol or phenol group through an ester linkage. The analogues were synthesized by a lipase-catalyzed esterification of phenols having a primary alcohol (**1**~**3**) with unsaturated fatty acids of different number of double bonds (**4**) (Scheme 1). *Pseudomonas cepacia* lipase catalyzed the regioselective acylation of the primary aliphatic hydroxy group in **1**~**3** to produce the urushiol analogues having no rash-causing properties. In our new approach, the analogues were obtained by one or two reaction steps via facile pro-



Scheme 1

cedures from commercially available reagents, whereas urushiol synthesis involved multi-step reaction pathways mainly owing to difficulty of the direct introduction of the unsaturated group onto the phenolic aromatics; blocking and deblocking of the phenol moiety are often required.

For the curing, used was laccase derived from *Pycnoporus coccineus* as catalyst, which was highly active for the oxidative polymerization of 2,6-dimethylphenol and syringic acid to give poly(1,4-phenylene oxide).[25),27),28)] Laccase belongs to an oxidoreductase having a copper-protein moiety as active site.[10)] The curing of **5**~**7** was performed in the presence of acetone powder (AP, an acetone-insoluble part of the urushi sap containing mainly polysaccharides and glycoproteins) with 80% humidity at 30 °C for 24 h. AP, a third component of the sap in addition to an urushiol and laccase, is believed to act as emulsifier of oily urushiol and aqueous laccase solution. The sample film was prepared on a glass slide by using applicator for 50 μm thickness. The crosslinked film was obtained from **6b**, **6c**, **7b**, and **7c**, and other urushiol analogues were not cured. In the curing without laccase (control experiment), the film formation was not observed. These data indicate that the present curing took place via the enzymatic catalysis and catechol or 2-methoxyphenol moiety having two or three unsaturated groups in the side chain was required for the hardening. The crosslinking of **6** proceeded faster than that of **7**.

The curing of **6c** was monitored by using a dynamic microhardness tester (Fig. 1). At the initial stage of the curing, the hardness value was very small and the sudden increase was observed after two weeks. Later, the value gradually increased to reach. ca. 150 N/mm^2 after 5 weeks. The gloss value of the film surface was more than 100. The pencil scratch hardness reached H after 15

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*) A suggestion was made to use "man-made urushi" rather than "artificial urushi" for the present study.

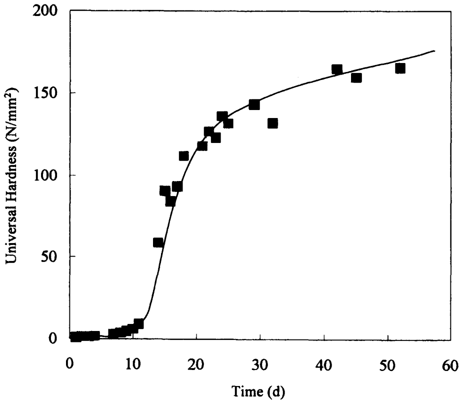
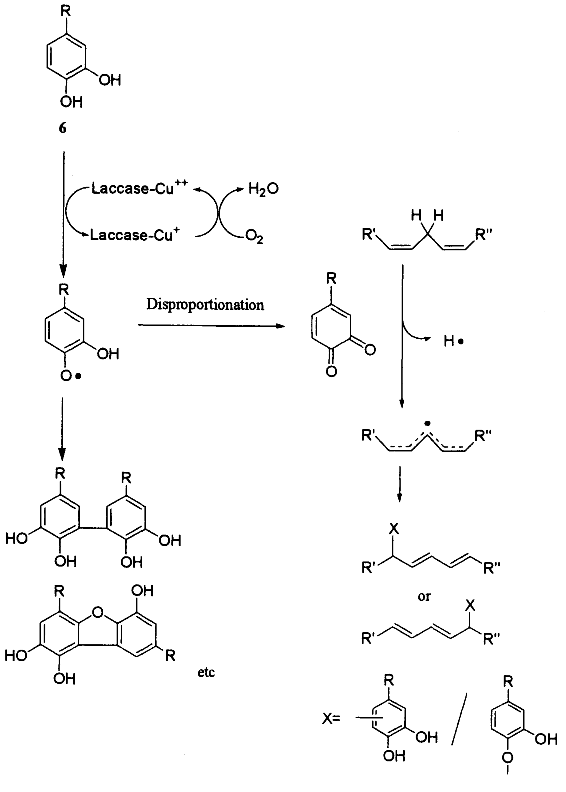


Fig. 1. Time course in hardening of man-made urushi film from **6c** by using Fischer microhardness tester.

days, which is hard enough for practical uses. The hardness and gloss values of the present cured film are comparable to those of natural urushi coating; the curing of the urushiol analogues produced the brilliant film with the high gloss surface. In the curing of **6b** in the presence of AP, on the other hand, the hardness value was less than 5 N/mm^2 after 6 weeks. The reaction monitoring by FT-IR showed that the present curing of **6** proceeds via the oxidative coupling of the phenol moiety of **6** and the subsequent autoxidation of the unsaturated group in the side chain (Scheme 2).[8)]

Recently, starch-urea phosphate (SP), a synthetic material, was reported to be highly effective as the third component for *in vitro* enzymatic curing of urushiols.[29)] In the curing of **6b** and **6c** in the presence of SP which is a substitute of AP (the natural sap component), the polymeric film was also obtained. However, the film hardness from **6c** was much smaller than that using AP as the third component. Interestingly, the curing of **6b** in the presence of SP produced the crosslinked film with relatively good hardness (30 N/mm^2 after 10 weeks); only a soft film was obtained by curing of **6b** in the presence of AP. Using SP as the third component provided the artificial urushi from exclusively synthetic compounds.

Fig. 2 shows storage modulus (E′) and dissipation factor (tan δ) of the cured films from **6c** as a function of temperature. In case of the sample obtained in the presence of AP after drying for 5 months, the glass transition temperature (Tg) was observed at 102 °C (Fig. 2(A)). The increase of E′ in the region of high temperature indicates that the unreacted unsaturated carbon-carbon double bonds remained in the measured sample. Smooth trace of tan δ means the homogeneous structure



Scheme 2

of the present cured film, suggesting the good miscibility between the urushiol analogue and AP. Similar traces were observed in the sample prepared by using SP as the third component (Fig. 2(B)). These dynamic elastic behaviors of the man-made urushi were very similar to those of natural urushi (Fig. 2(C)).

Preparation of crosslinkable polyphenols from urushiol analogues.[21)] As described above, urushiol analogue **5** was not cured via laccase catalysis. Thus, we have examined preparation of another "man-made urushi" by an oxidative polymerization of **5**, followed by curing of the resulting crosslinkable polyphenols (Scheme 3).

Here, iron-N,N'-ethylenebis(salicylideneamine) (Fe-salen) was used as catalyst for the oxidative polymerization of **5**. We regarded Fe-salen as model complex of peroxidase having a heme as catalytic active site. It was reported that the Fe-salen complex showed high catalytic activity toward an oxidative polymerization of 2,6-dimethylphenol and p-t-butylphenol to produce the soluble polymers.[30),31)] Furthermore, we have first synthesized crystalline fluorine-containing poly(phenylene oxide) by the Fe-salen-catalyzed polymerization of 2,6-difluorophenol.[32)]

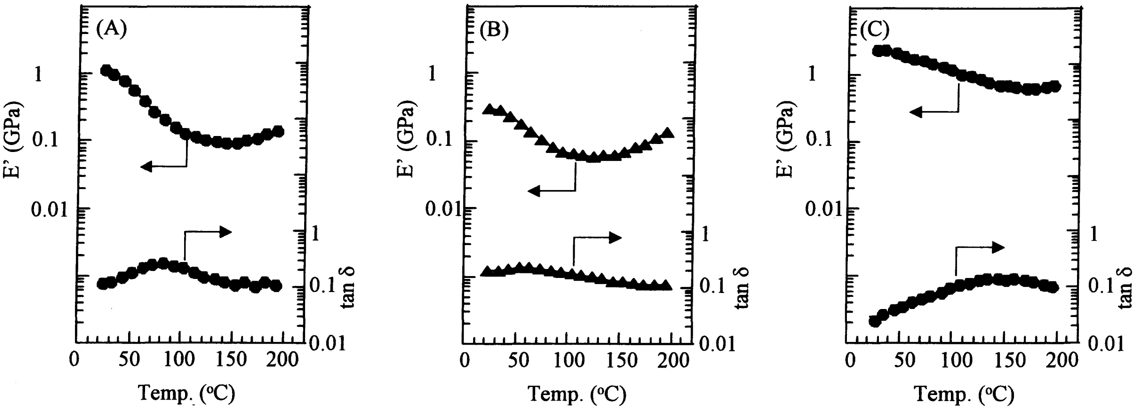
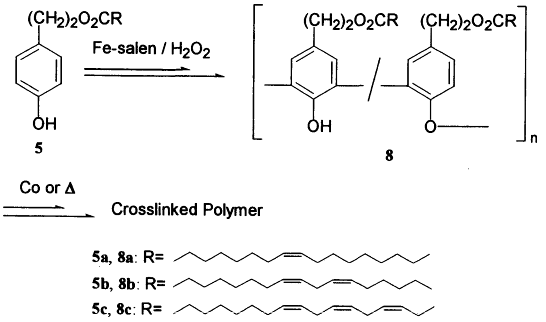


Fig. 2. Dynamic viscoelasticity of (A) man-made urushi obtained from **6c** in the presence of AP; (B) that from **6b** in the presence of SP, and (C) natural urushi.



Scheme 3

The polymerization of **5** catalyzed by Fe-salen was performed using hydrogen peroxide as oxidizing agent in tetrahydrofuran (THF) at room temperature under air. After the polymerization, the reaction mixture was poured into a large amount of methanol to give an oily precipitate, which was collected by centrifugation. ^{1}H NMR analysis of **8** showed that the unsaturated moiety was not reacted during the polymerization.

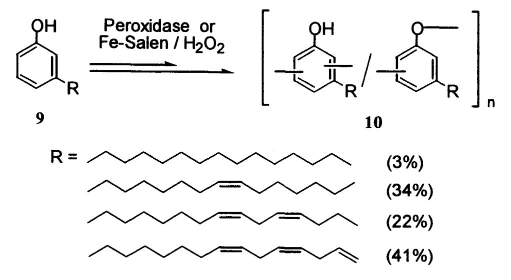
Polymerization of **5a** produced soluble polymer **8a** with molecular weight of several thousands, whose index was relatively small (< 2). On the other hand, molecular weight and its index of polymers **8b** and **8c** were larger than those of **8a**; in some cases, the molecular weight was beyond 1×10^4. Futhermore, **8c** became partly insoluble in the high loading of the catalyst. These data showed that the crosslinking between the unsaturated groups in the side chain of **8b** or **8c** partly took place, resulting in the increase of the molecular weight distribution value and/or the formation of the insoluble products.

The curing of the polymers was examined by two methods: oxidation catalyzed by cobalt naphthenate (3 weight-% for **8**) in air and thermal treatment (150 °C for 2 h). The sample film prepared on a glass slide stood at 25 °C under the humidity of 70%.

In the case of **8b** and **8c**, the hardness value of the film with thermal treatment was ca. 100 N/mm^2 after 3 days. The hardness of the cured film of **8c** gradually increased and reached more than 140 N/mm^2 after 4 weeks, whereas the hardness of the cured film of **8b** was almost constant. In the curing by cobalt naphthenate catalyst, **8b** and **8c** were also cured, however, the curing proceeded more slowly than the thermal curing. The formation of the cured film from **8a** was not observed in both curing methods. These data indicate that two or three unsaturated group in the side chain was required for the hardening. The surface gloss value of the cured film obtained by using cobalt naphthenate catalyst was more than 100, indicating the formation of the film with the high gloss surface.

Preparation of crosslinked polymeric film from cardanol.[22)-25)] Cardanol (**9**) can also be taken as an urushiol analogue. **9**, a main component obtained by thermal treatment of cashew nut shell liquid (CNSL), is a phenol derivative mainly having the meta substituent of a C15 unsaturated hydrocarbon chain mainly with 1-3 double bonds. Since CNSL is nearly the one third of the total nut weight, much amount of CNSL is formed as by-product from mechanical processes for the edible use of the cashew kernel. Only a small part of **9** obtained in the production of cashew kernel is used in industrial field, though it has various potential industrial utilizations such as resins, friction lining materials, and surface coatings. Therefore, development of new applications for **9** is strongly desired.

Phenolic resins from **9** and formaldehyde are industrially produced as prepolymer of coating materials



Scheme 4

Table I. Oxidative polymerization of cardanol using Fe-salen catalyst in bulk[a]

Entry	Catalyst amount (%)[b]	Time (h)	Yield (%)[c]	Mn[d]	Mw/Mn[d]
1	0.50	2.0	38	1400	1.6
2	1.0	0.50	70	2800	2.8
3	1.0	2.0	70	3000	3.0
4	1.5	2.0	80	2900	4.5
5	2.0	2.0	Gelation		

[a] Polymerization of cardanol (6.0 g) using hydrogen peroxide (30%, 2.1 mL) in the presence of Fe-salen catalyst under air. [b] Molar ratio of Fe-salen for **9**. [c] Methanol-insoluble part. [d] Determined by SEC using THF eluent, calibrated with polystyrene standards.

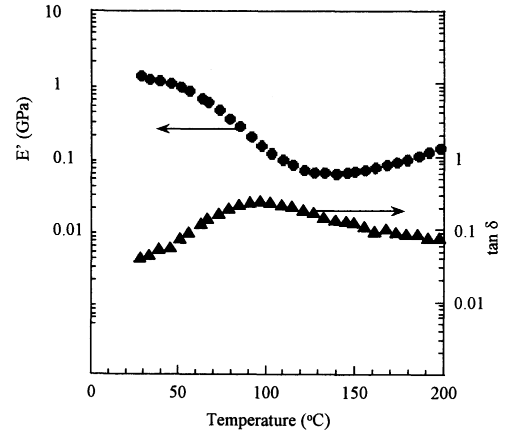


Fig. 3. Dynamic viscoelasticity of crosslinked film of poly(cardanol).

with high gloss surface mainly for indoor use. However, resins containing formaldehyde have much concern about toxic nature of formaldehyde in their manufacture and use. We have examined synthesis and curing of polymer **10** obtained by a peroxidase-catalyzed oxidative polymerization of **9** (Scheme 4). This curing reaction is regarded as a new formaldehyde-free coating system from **9**.

We have reported that horseradish and soybean peroxidases (HRP and SBP, respectively) were efficient catalysts for oxidative polymerization of various phenol derivatives.[10)–12)] As for the polymerization of **9**, SBP showed high catalytic activity to give the oily polymer with molecular weight of several thousands, whereas the polymerization did not occur via HRP catalysis. A similar behavior was observed in peroxidase-catalyzed polymerization of m-substituted phenols; SBP could readily polymerize the monomer having a large substituent, whereas in the case of small substituent monomers, the high yield was achieved by using HRP catalyst.[33)]

Polymer structure was confirmed by ^{1}H NMR spectroscopy. The peaks' pattern of **10** was similar to that of **9**, although all the peaks of **10** were broader than those of **9**. The integrated area ratio of peaks due to unsaturated and saturated groups in the side chain did not change before and after the polymerization, indicating that the unsaturated group was not reacted and only the phenolic moiety was polymerized. FT-IR analysis of the polymer supported no reaction of the unsaturated group during the polymerization.

Fe-salen also catalyzed the polymerization of **9** in organic solvents as well as bulk. Using 1,4-dioxane as solvent gave the soluble polymer in good yields and the addition of pyridine improved the polymer yield and molecular weight. The polymerization also proceeded without organic solvent to produce the polymer (Table I). When the catalyst amount was 1.0 or 1.5% for **9**, the soluble polymer was obtained in relatively high yields. On the other hand, the higher loading of the catalyst resulted in the gelation (entry 5).

The curing was examined by similar method of **8**: catalysis of cobalt naphthenate (3 weight-% for **10**) and thermal treatment (150 °C for 30 min). As for the sample obtained by Fe-salen catalyst, the curing of **10** took place within 1 h in both methods to give a yellow transparent film which can also be regarded as "man-made urushi" in a broader sense. On the other hand, such a quick hardening was not observed in monomer **9**. These data indicate that **10** was a good crosslinkable prepolymer. The hardness of the film cured by the cobalt catalyst reached nearly 100 N/mm^2 after 7 days. The gloss value of the film surface was higher than 100. These values are comparable to those of cardanol-formaldehyde coating materials. The resulting crosslinked film exhibited good elastic properties and its Tg was relatively high (ca. 100 °C) (Fig. 3). The curing of the enzymatically obtained poly(cardanol) also proceeded by cobalt naphthenate catalyst to gave the crosslinked film with good hardness. FT-IR monitoring of the curing of **10** showed that the crosslinking mechanism was similar to that of the oil autoxidation.

Conclusion. In conclusion, "man-made urushi" with high gloss surface and good elastic properties has been developed by enzymatic crosslinking of new urushiol analogues, catechol derivatives having two or three unsaturated group in the higher alkyl side chain, under mild reaction conditions without use of organic solvents. The present enzymatic curing to functional polymeric materials expanded the scope of enzymatic polymerizations. Crosslinked polymeric film with good hardness was also obtained by the oxidative polymerization of another urushiol analogues using Fe-salen as catalyst, followed by curing via an autoxidation mechanism. The oxidative polymerization of cardanol produced a good prepolymer for the curing. In all cases, the resulting crosslinkable prepolymers were prepared from cheap plant-based oils, one of the most important renewable resources, without use of toxic formaldehyde. In the curing stage, the crosslinked polymeric film is obtained in the absence of organic solvents at an ambient temperature under air. Therefore, the present method has large potential for a future environmentally-benign process of polymer coating.

Acknowledgements. This work was supported by a Grant-in-Aid for Specially Promoted Research (No. 08102002) from the Ministry of Education, Science, Sports and Culture of Japan, and from NEDO for the project on Technology for Novel High-Functional Materials in Industrial Science and Technology Frontier Program, AIST, Japan.

References

1) Rague, B. V. (1976) A History of Japanese Lacquer Work, University of Toronto Press, Toronto.
2) Kumanotani, J. (1983) In Polymer Application of Renewable Resource Materials (eds. Carraher, C. E., and Sperling, L. H). Plenum Press, New York, pp. 225-248.
3) Snyder, D. M. (1989) J. Chem. Educ. **66**, 977-980.
4) Majima, R. (1909) Ber. Dtsch. Chem. Ges. **42B**, 1418-1423.
5) Majima, R. (1922) Ber. Dtsch. Chem. Ges. **55B**, 172-191.
6) Majima, R. (1922) Ber. Dtsch. Chem. Ges. **55B**, 191-214.
7) Kasamori, M., Sakamoto, M., Awazu, K., Ichikawa, T., and Egashira, T. (1966) In The Polymeric Materials Encyclopedia (ed. Salamone, J. C.). CRC Press, Boca Raton, pp. 3499-3504.
8) Kumanotani, J. (1996) In The Polymeric Materials Encyclopedia (ed. Salamone, J. C.). CRC Press, Boca Raton, pp. 4835-4842.
9) Terada, M., Oyabu, H., and Aso, Y. (1994) J. Jpn. Soc. Colour Mater. **67**, 681-687.
10) Kobayashi, S., Shoda, S., and Uyama, H. (1997) In Catalysis in Precision Polymerization (ed. Kobayashi, S.). John Wiley & Sons, Chichester, Chapter 8.
11) Kobayashi, S. (1999) J. Polym. Sci., Polym. Chem. Ed. **37**, 3041-3056.
12) Kobayashi, S., and Uyama, H. (1998) In Materials Science and Technology, Synthesis of Polymers (ed. Schlüter, A.-D.). Wiley-VCH, Weinheim, Chapter 16.
13) Kobayashi, S., Shoda, S., and Uyama, H. (1995) Adv. Polym. Sci. **121**, 1-30.
14) Gross, R. A., Kaplan, D. L., and Swift, G. (ed.) (1998) ACS Symp. Ser. **684**.
15) Ritter, H. (1977) In Desk Reference of Functional Polymers, Syntheses and Applications (ed. Arshady, R.). American Chemical Society, Washington, pp. 103-113.
16) Uyama, H., Lohavisavapanich, C., Ikeda, R., and Kobayashi, S. (1998) Macromolecules **31**, 554-556.
17) Tonami, H., Uyama, H., Kobayashi, S., Fujita, T., Taguchi, Y., and Osada, K. (2000) Biomacromolecules **1**, 149-151.
18) Mohanty, A. K., Misra, M., and Hinrichsen, G. (2000) Macromol. Mater. Eng. **276/277**, 1-24.
19) Kobayashi, S., Ikeda, R., Oyabu, H., Tanaka, H., and Uyama, H. (2000) Chem. Lett., pp. 1214-1215.
20) Ikeda, R., Tanaka, H., Oyabu, H., Uyama, H., and Kobayashi, S. Bull. Chem. Soc. Jpn. (in press).
21) Tsujimoto, T., Ikeda, R., Uyama, H., and Kobayashi, S. (2000) Chem. Lett., pp. 1122-1123.
22) Ikeda, R., Tanaka, H., Uyama, H., and Kobayashi, S. (2000) Macromol. Rapid Commun. **21**, 496-499.
23) Ikeda, R., Tanaka, H., Uyama, H., and Kobayashi, S. (2000) Polym. J. **32**, 589-593.
24) Uyama, H., and Kobayashi, S. (1999) CHEMTECH **29(10)**, 22-28.
25) Uyama, H., Ikeda, R., Yaguchi, S., and Kobayashi, S. (2000) ACS Symp. Ser. **764**, 113-127.
26) Kobayashi, S. (1999) High Polymers, Jpn. **48**, 124-127.
27) Ikeda, R., Uyama, H., and Kobayashi, S. (1996) Macromolecules **29**, 3053-3054.
28) Ikeda, R., Sugihara, J., Uyama, H., and Kobayashi, S. (1996) Macromolecules **29**, 8702-8705.
29) Oyabu, H., Terada, M., Aso, Y., and Oda, Y. (1995) J. Jpn. Soc. Colour Mater. **68**, 729-734.
30) Tonami, H., Uyama, H., Kobayashi, S., Higashimura, H., and Oguchi, T. (1999) J. Macromol. Sci.-Pure Appl. Chem. **A36**, 719-730.
31) Tonami, H., Uyama, H., Higashimura, H., Oguchi, T., and Kobayashi, S. (1999) Polym. Bull. **42**, 125-129.
32) Ikeda, R., Tanaka, H., Uyama, H., and Kobayashi, S. (2000) Macromolecules **33**, 6648-6652.
33) Tonami, H., Uyama, H., Kobayashi, S., and Kubota, M. (1999) Macromol. Chem. Phys. **200**, 2365-2371.