Macromolecules **1988,** *21,* 1579–1583 **1579**

and St has to play an exclusive role in this addition, indicating one of the features of the alternating copolymerization.

For the case of the terpolymerization of TMCQ (TECQ), TCNQ, and St, since TCNQ is the most highly conjugative (reactive) monomer, the polymer radicals of terminal monomer unit other than TCNQ unit react exclusively with TCNQ due to their reaction energetic profiles and the resulting polymer radical of terminal TCNQ unit reacts with either TMCQ (TECQ) or St under favor of strong charge-transfer interaction between the polymer radical and the monomers. Therefore, the terpolymer always consists of 50 mol % of TCNQ unit regardless of monomer feed ratios. Probably this is a reasonable explanation.

Finally, a new concept is proposed on the mechanism of the radical alternating copolymerization as follows: (1) The first point is the fact that the more highly conjugative (reactive) monomer between copolymerizable monomer pair is not homopolymerizable, probably due to participation of the depolymerization. (2) The second point is the fact that the resulting polymer radical, which is considered as very stable, unreactive, undergoes cross propagation under favor of strong charge-transfer interaction with the comonomer due to a great difference in polarity between the two reacting species, corresponding to the rate-determining process of the alternating copolymerization. The reactivity of the alternating copolymerization is different from that of the conventional radical copolymerization and is determined exclusively with the polar character of the polymer radical and the monomer.

Registry No. BzCQ, 110458-74-7; AcCQ, 110458-72-5; BCQ, 99214-01-4; AIBN, 78-67-1; (BzCQ)(St) (alternating copolymer), 114132-86-4; (AcCQ)(St) (alternating copolymer), 114132-88-6; (BCQ)(St) (alternating copolymer), 114132-89-7; St, 100-42-5.

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Studies on Chitin. 13. New Polysaccharide/Polypeptide Hybrid Materials Based on Chitin and Poly(γ-methyl L-glutamate)

Keisuke Kurita,* Akira Yoshida, and Yoshiyuki Koyama

Department of Industrial Chemistry, Faculty of Engineering, Seikei University, Musashino-shi, Tokyo, Japan.

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ABSTRACT: A new type of polysaccharide/polypeptide hybrid material, chitin derivatives having polypeptide side chains, was prepared by the graft copolymerization of γ-methyl L-glutamate *N*-carboxy anhydride (NCA) onto water-soluble chitin in water/ethyl acetate. The polymerization proceeded quite smoothly, and both the conversion and grafting efficiency were very high owing to the homogeneous polymerization conditions which became feasible by making use of the water-soluble characteristic of the partially deacetylated chitin. The length of the polypeptide chains was easily regulated by the amount of NCA, and the graft copolymers with side chains of various lengths were obtained reproducibly. The results of solubility tests, infrared spectroscopy, and X-ray analysis of the copolymers were largely dependent on the side-chain length, and influence of α-helix formation by the side chains was evident. The ester groups of the side chains were transformed into carboxylate groups by alkaline hydrolysis, and the resulting copolymers exhibited remarkable water solubility.

Introduction

Chitin is the most abundant natural amino polysaccharide and estimated to be produced annually almost as much as cellulose. It has become of great interest not only as an underutilized resource but as a new functional material of high potential in various fields, and the recent progress in chitin chemistry is quite noteworthy. Special attention has been given to the chemical modifications of chitin as one of the most probable means to realize its full potential. Reactions with chitin have been carried out mostly on solid chitin owing to the lack of solubility in ordinary solvents. A partially deacetylated chitin with about 50% deacetylation prepared by homogeneous hydrolysis was, however, found to be soluble in water.[1,2] This water-soluble chitin has a great advantage as a starting material for modifications, since the water solubility allows smooth reactions under mild conditions.

We have attempted to develop various modes of efficient modification reactions on chitin.[3–8] Among the modifications yet undeveloped, graft copolymerization on chitin is very attractive, being capable of affording novel hybrid materials based on this polysaccharide, although only a few papers reported the graft copolymerization on chitin, using vinyl monomers, with low grafting efficiencies.[9,10] In a

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Scheme I

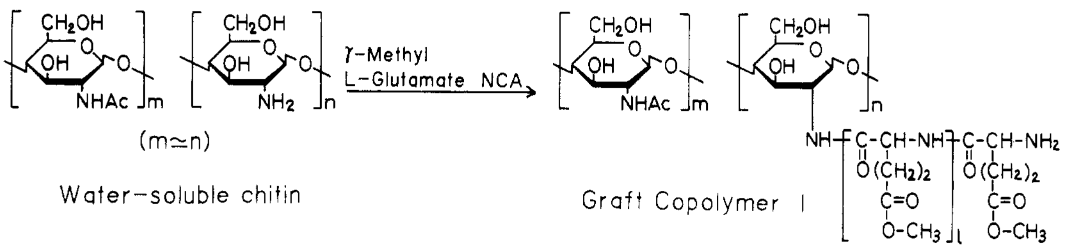


Table I
Graft Copolymerization of γ-Methyl L-Glutamate NCA onto Water-Soluble Chitin

chitin,[a] g	NCA, g	NCA (mol)/ NH_2 (mol)	yield, g	DP of polypeptide side chains[b]		conversion,[e] %	
				weight[c]	IR[d]	weight	IR
0.50	0.50	1.9	0.81	1.6	1.5	84	79
0.50	0.56	2.3	0.89	2.1	1.8	91	78
0.50	1.21	4.9	1.24	4.0	3.2	82	65
0.50	2.12	8.4	1.66	6.2	6.0	73	71
0.50	2.43	9.9	2.16	8.8	7.2	89	73
0.50	3.35	13.6	2.45	10.4	10.9	76	80
0.50	4.12	16.1	3.06	13.1	12.3	81	76
0.50	7.59	26.6	5.31	22.0	20.8	83	78

[a] Water-soluble chitins with 48–55% deacetylation were used. [b] Average degree of polymerization. [c] Determined from weight increase. [d] Determined with a calibration curve based on IR spectroscopy. [e] Amount of NCA polymerized/amount of NCA added.

previous paper,[11] we showed the possibility of preparing chitin–protein complexes by the graft copolymerization of an amino acid *N*-carboxy anhydride (NCA) onto chitin. Water-soluble chitin was found to be very promising for this sensitive reaction with the NCA since it made possible the reaction in solution and thus the amino groups readily accessible. Aiba and co-workers also reported the graft copolymerization on chitosan under heterogeneous conditions recently.[12] The resulting materials, polysaccharide/polypeptide complexes, are expected to be useful as biocompatible materials, chromatography adsorbents, membrane materials, and supports for bioactive species as well as models for naturally occurring chitin which has covalently linked polypeptide chains at some of the amino groups.[13]

In this paper, we report the results of the highly efficient graft copolymerization of γ-methyl L-glutamate NCA onto water-soluble chitin and some properties of the resulting chitin derivatives having polypeptide side chains.

Experimental Section

Materials. Water-soluble chitin was prepared according to the method already reported.[1] γ-Methyl L-glutamate NCA was synthesized by treating γ-methyl L-glutamate with 0.6 molar equiv of trichloromethyl chloroformate[14] in tetrahydrofuran for 2 h at 40 °C. Recrystallization from ethyl acetate gave white crystals, yield 76%, mp 99–100 °C.

Graft Copolymerization. The graft copolymerization of γ-methyl L-glutamate NCA onto chitin was carried out in a similar manner to that described in the previous paper.[11] A given amount of the NCA, dissolved in 10 mL of dry ethyl acetate (15 mL for 26.6 molar equiv of NCA), was subjected to the reaction with 0.50 g of water-soluble chitin in 50 mL of water at 0 °C for 2 h. The resulting graft copolymer 1 was coagulated in 650 mL of dimethylformamide (DMF). Water, 60 mL, was added, and the precipitate was filtered. It was washed thoroughly with DMF/water (13:1) and then with acetone and dried under vacuum.

Hydrolysis of the Ester Groups of Graft Copolymers 1. A dispersion of 0.50 g of a graft copolymer 1 with polypeptide side chains of an average degree of polymerization of 10.4 in 50 mL of 1 M sodium carbonate was stirred at 70 °C for 1 h. The resulting clear solution was dialyzed for 2 days against deionized water. It was concentrated to a few milliliters and then freeze-dried to give 0.42 g of graft copolymer **2** as a white powdery material.

Measurements. Infrared spectra were taken with JASCO A-320 and A-1 spectrophotometers. X-ray diffraction diagrams were recorded on a Rigaku RAD-IA by the powder method with the use of nickel-filtered Cu Kα radiation.

Results and Discussion

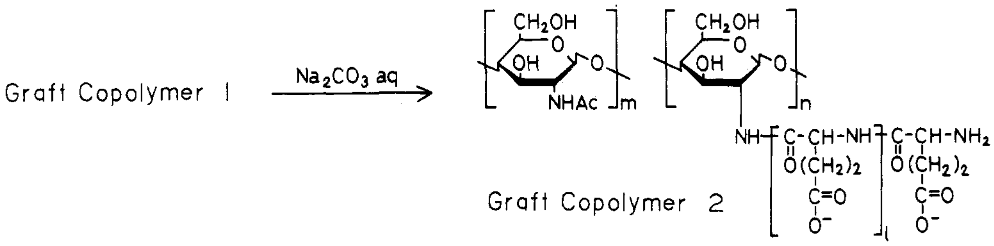
Graft Copolymerization. Solution reaction under mild conditions is essential for efficient modification of chitin, especially for the graft copolymerization of an amino acid NCA which undergoes side reactions under severe conditions. The reaction of water-soluble chitin in water and γ-methyl L-glutamate NCA in ethyl acetate was carried out with cooling at 0 °C to suppress side reactions of the NCA. Although NCA is very susceptible to hydrolysis, the amino groups of chitin attacked the NCA smoothly in solution to give the graft copolymer 1 with polypeptide side chains (Scheme I). As expected, the hydrolysis of the NCA to the amino acid and carbon dioxide was the only evident side reaction and no homopolypeptide was detected under the conditions used. This was also confirmed by a control reaction in the absence of water-soluble chitin when only the amino acid was recovered in 90–95% yield without any evidence of homopolypeptide formation.

With a view to preparing graft copolymers having polypeptide side chains of various lengths, the amount of NCA added was varied over the range 1.9–26.6 molar equiv per amino group of water-soluble chitin. The reaction with more than 10 equiv of the NCA resulted in the immediate formation of a gelatinous white precipitate, but that with a smaller amount of NCA gave a white suspension in 2 h. The resulting graft copolymers were isolated in a mixture of DMF and water; these solvents were useful for removing the homopolypeptide, if any formed, and the amino acid.

The results of the graft copolymerization experiments are summarized in Table I. The yield of the copolymer increased with an increase in the amount of NCA added, indicating the introduction of polypeptide side chains of increasing length. The average degrees of polymerization (DPs) of the polypeptide chains were calculated from weight increases, and the results are included in Table I. They were in the range 2–22.

The side-chain lengths were also determined by infrared spectroscopy on the basis of the absorbance at 1730 cm^{-1}

Scheme II



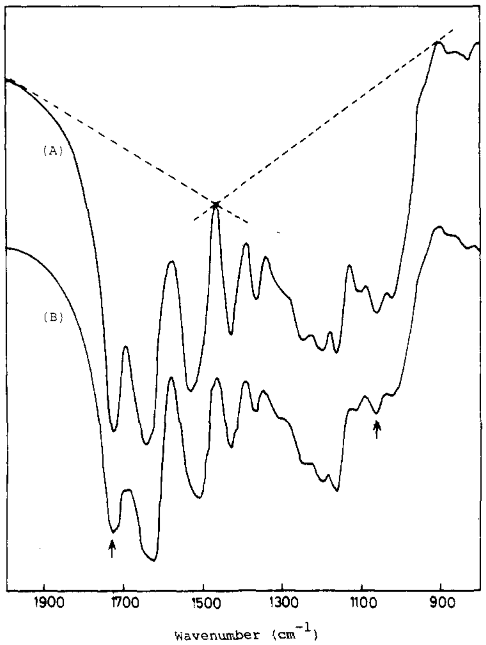


Figure 1. Infrared spectra of (A) graft copolymer 1 (DP = 7) and (B) a mixture of the homopolymers (peptide units/amino group = 8) (KBr).

of the ester groups in the side chains compared with that at 1060 cm^{-1} of the pyranose rings in the water-soluble chitin component. A calibration curve was drawn by using the spectra of mixtures of various ratios of water-soluble chitin and homopoly(γ-methyl L-glutamate). A typical example of the spectra of the mixtures along with that of the corresponding graft copolymers 1 is demonstrated in Figure 1 where the base lines for the absorbance determination are shown. Figure 2 shows the calibration line, the dependence of the absorbance ratio A_{1730}/A_{1060} on the mixing ratio of the two homopolymers. The numbers on the abscissa indicate the amount of peptide units per amino group of the water-soluble chitin, hence the average DP of polypeptide chains in the graft copolymers. The DPs determined by this calibration line are also listed in Table I. The values are in good agreement with those calculated from the weight increases. These results were quite reproducible, thus indicating that the length of the polypeptide side chains can be regulated easily by varying the amount of NCA under these conditions.

The grafting conversion, which is the ratio of the amount of NCA graft copolymerized to that fed in the reaction, was calculated on the basis of the DPs by both the weight increases and infrared spectroscopy. The values were considered to be very high in all cases (Table I), taking into account the susceptibility of the NCA to hydrolysis. The grafting efficiencies were supposed to be almost 100%, since homopolypeptide was never detected. The graft copolymerization was thus confirmed to proceed quite efficiently, primarily because of the solution graft copolymerization using water-soluble chitin.

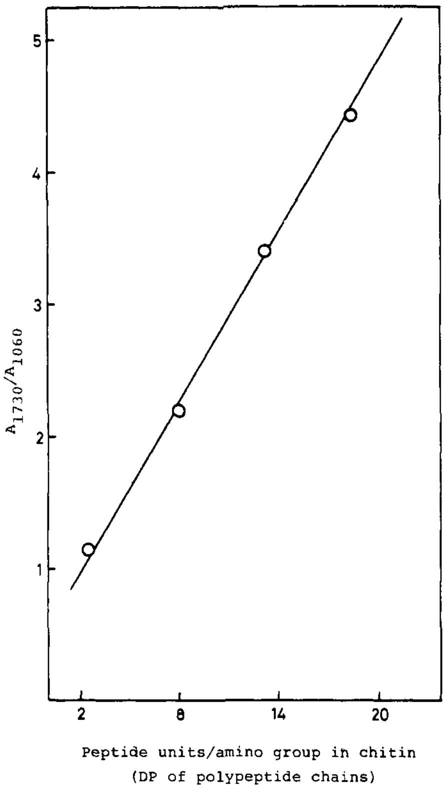


Figure 2. Calibration line based on the mixtures of the homopolymers.

The products were white or off-white powdery materials and readily soluble in hexafluoro-2-propanol to give viscous clear solutions. Films could be obtained by casting the solutions and drying; they were tough, flexible, and transparent.

Hydrolysis of Graft Copolymers 1. The γ-methyl ester groups in the side chains were then hydrolyzed to afford derivatives having carboxylate groups which would show good solubility in water. When powdered graft copolymer 1 was treated with 1 M sodium hydrogen carbonate, the mixture still contained the solid copolymer after 1.5 h at 90 °C, and the removal of the ester groups appeared to be incomplete judging from the infrared spectra. The alkaline solution was then replaced by 1 M sodium carbonate, where the graft copolymer went into solution in around 40 min at 70 °C, and no ester bands were found in the infrared spectra after 1 h. After dialysis and freeze-drying, hydrolyzed graft copolymer 2 was obtained in a sodium salt form as a white powdery material (Scheme II).

Amide linkages may also be cleaved by this alkaline treatment. Water-soluble chitin, however, showed no reduction in the acetyl content under the same conditions, and thus the peptide bonds in the side chains as well as the acetamido groups on the backbones seem not to suffer hydrolysis to an appreciable extent in this step.

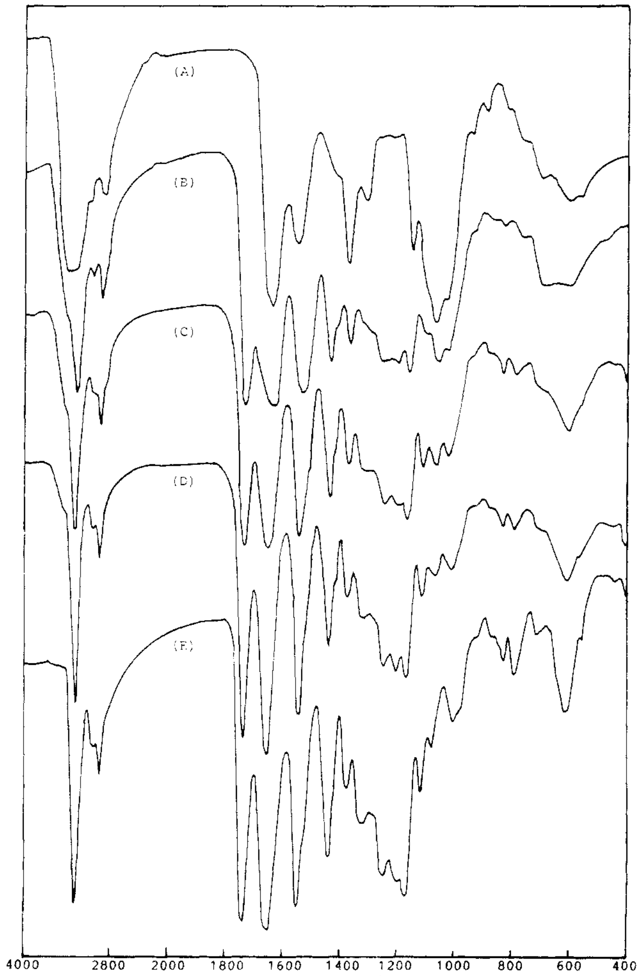


Figure 3. Infrared spectra of the films of (A) water-soluble chitin, (B) graft copolymer 1 (DP = 4), (C) graft copolymer 1 (DP = 10), (D) graft copolymer 1 (DP = 22), and (E) poly(γ-methyl L-glutamate).

Infrared Spectroscopy. Some typical infrared spectra of the films of water-soluble chitin, graft copolymers 1, and homopoly(γ-methyl L-glutamate) are illustrated in Figure 3. The appearance of a strong ester band at 1730 cm^{-1} is the most characteristic of original graft copolymers 1. The absorbances of the ester band and amide bands I (1650 cm^{-1}) and II (1550 cm^{-1}) increases and that of the pyranose bands (1000–1150 cm^{-1}) decreases with an increase in the length of the polypeptide side chains compared to those of the starting water-soluble chitin. A broad band at 3350 cm^{-1} of the water-soluble chitin becomes sharp as a result of the graft copolymerization and the shape changes continuously, becoming similar to that of the homopolypeptide as the side-chain length increased. The band at 610 cm^{-1}, ascribable to the α-helix structure of poly(γ-methyl L-glutamate), becomes evident in the spectra of the graft copolymers with side chain DPs around 10, and the absorbance increases with DP. The ester band of graft copolymer 1 disappeared completely on alkaline hydrolysis and a carboxylate band is observed at 1560 cm^{-1} in the spectrum of graft copolymer 2.

X-ray Diffraction. Graft copolymers 1 were subjected to X-ray diffraction analysis to see the change in crystallinity. As shown in Figure 4, much difference is not observed except the appearance of a peak at $2\theta = 8.3°$, which is assignable to the α-helix structure of poly(γ-methyl L-glutamate). As expected, the peak intensity increases with an increase in the side-chain length, and the graft copolymer with a side-chain DP of 20 exhibited a distinct peak. This is consistent with the infrared spectral observation that graft copolymers 1 with DPs above a certain limit showed an α-helix band at 610 cm^{-1}.

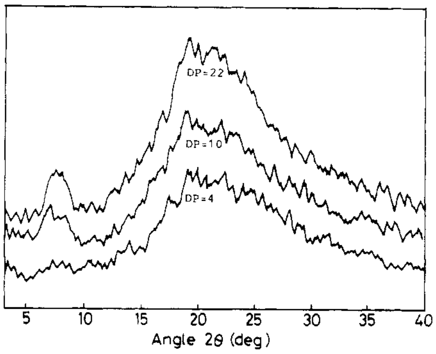


Figure 4. X-ray diffraction diagrams of graft copolymers 1.

Solubility. Qualitative solubilities of graft copolymers 1 and graft copolymers 2 were examined in comparison with those of water-soluble chitin in excess solvents at room temperature. All of graft copolymers 1 were soluble in dichloroacetic acid in addition to hexafluoro-2-propanol but insoluble in ordinary aprotic polar solvents such as DMF, dimethylacetamide (DMAc), and hexamethylphosphoramide (HMPA). DMAc containing lithium chloride appeared to be a somewhat better solvent, but only low swelling was observed. Dimethyl sulfoxide (DMSO), however, exhibited higher affinity for graft copolymers 1 than the other aprotic solvents. Although water-soluble chitin and graft copolymers 2 did not swell much in DMSO, a graft copolymer 1 with the side chains of DP = 2 swelled considerably. Furthermore, that of DP = 4 showed extremely high swelling and was almost soluble. The swelling ability in DMSO then decreased with increasing DP, and the copolymers having long polypeptide chains swelled only very slightly. This change in swelling behavior is noteworthy and may be ascribable to the formation of the ordered structures of the polypeptide chains including the α-helix. The polypeptide chains with low DPs cannot form α-helix structures and may simply act to disturb the contact arrangement of chitin molecules, leading to high swelling ability. When the DP increases, the chains start to form some ordered structures as suggested by both infrared spectroscopy and X-ray diffractiometry, resulting in poor affinity for the solvent. Graft copolymers 1 swelled to some extent in *m*-cresol; only those with low DPs swelled also in aqueous acetic acid.

Graft copolymers 2 showed better solubility and were soluble in *m*-cresol in contrast to the poor swelling or insolubility of 1 and water-soluble chitin. Dichloroacetic acid is a good solvent for 2 as well as for water-soluble chitin. Although graft copolymers 1 were insoluble in water, both water-soluble chitin and graft copolymers 2 were soluble in water. The most striking characteristic is that the latter exhibited quite high solubility and was readily soluble in water at all temperatures tested, whereas the former can be dissolved in water by stirring with crushed ice at 0 °C in an ice bath over a few hours.[1] Aqueous acetic acid is a much better solvent than water for water-soluble chitin but not for graft copolymers 2 due to the protonation of the carboxylate groups, giving rise to insolubility.

These solubility characteristics along with other results support unambiguously the formation of graft copolymers and exclude the possibility that they are mixtures of homopolymers.

Consequently, γ-methyl L-glutamate NCA was graft copolymerized onto chitin smoothly with remarkably high grafting efficiencies and also excellent reproducibility by making use of an advantage of the water-soluble nature of the partially deacetylated chitin. The polypeptide side-chain length, on which the solubility is greatly dependent, can be regulated easily. This method seems to be useful for preparation of various kinds of chitin/polypeptide hybrid materials.

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Registry No. γ-Methyl L-glutamate, 1499-55-4; γ-methyl L-glutamate NCA, 1663-47-4.

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Study of Polymeric Photosensitizer. 2. Syntheses of Multifunctional Polymeric Photosensitizers Containing a Pendant Nitroaryl Group and a Quaternary Phosphonium Salt and Their Application to the Photochemical Reaction of Potassium Cinnamate

Tadatomi Nishikubo,* Jiro Uchida, Kenkichi Matsui, and Takashi Iizawa

Laboratory of Polymer Chemistry, Faculty of Engineering, Kanagawa University, Rokkakubashi, Kanagawa-ku, Yokohama 221, Japan. *Received June 23, 1987*

ABSTRACT: Multifunctional polymeric photosensitizers containing both pendant nitroaryl groups as a photosensitizer moiety and pendant benzyltributylphosphonium chloride as a substrate-attracting group were synthesized by substitution reactions of poly((chloromethyl)styrene) (PCMS) with potassium salts of photosensitizing compounds by using phase-transfer catalysis followed by addition reactions of the resulting polymers with tributylphosphine (TBP) in *N,N*-dimethylformamide (DMF) under mild reaction conditions and by the addition reaction of PCMS with TBP followed by the substitution reaction of the potassium salt of the photosensitizing compound under the same reaction conditions. These reactions proceeded very smoothly to give the corresponding new multifunctional polymeric photosensitizers. One of the same polymeric photosensitizers was also prepared in 51% yield by radical copolymerization of the corresponding monomers by using azobis(isobutyronitrile) in DMF. These polymers were soluble in water and methanol, and the polymeric photosensitizers containing pendant benzyltributylphosphonium chloride as a substrate-attracting group and pendant 4-nitrophenoxy (PTBP-NP) or 4-(4-nitrophenoxy)butylate moieties as a chromophore showed higher photosensitization efficiency than the corresponding low molecular weight photosensitizer for trans–cis photoisomerization of potassium cinnamate in water. Furthermore, it was found that although the multifunctional polymeric photosensitizer PTBT-NP has excellent efficiency, the control of content of pendant photosensitizer moiety in the polymer and of concentration of the photosensitizer in the reaction system is very important to get high efficiency.

Introduction

It is well-known that photosensitizers have been widely used in photochemical reactions such as isomerization, dimerization, and oxidation of organic compounds in solution and in photocrosslinking or photodegradation reactions of several polymers in the film state. Polymeric photosensitizers have also been interesting from the viewpoint of solar energy storage and exchange processes. Moser and Cassidy[1] have reported cis–trans photoisomerization of *cis*-1,3-pentadiene by poly(vinyl phenyl ketone) (PVPK). Leermakers and James[2] have also reported photochemical balance isomerization of norbornadiene (NBD) to quadricyclane (QDC) and isomerization of piperylene using PVPK. The first photooxidation using polymer-based sensitizers containing pendant rose bengal moiety has been reported by Blossey et al.[3-6] Recently, Schaap and co-workers[7,8] and Neckers and co-workers[9-13] have studied separately these photooxidations using several polymeric photosensitizers containing rose bengal moiety. Neckers et al.[14,15] also reported photodimerization of coumarin or indene, cycloaddition of benzo(*b*)thiophene to dichloroethylene, and isomerization of NBD to QDC using polymeric photosensitizer containing benzophenone moiety. Hautala et al.[16,17] have proposed a solar energy storage process using a NBD–QDC system with heterogeneous photosensitizers such as the crosslinked polystyrene and silica gel having pendant 4-(*N,N*-dimethylamino)benzophenone moiety. However, the efficiency of all these polymeric photosensitizers was generally comparable to or slightly lower than the corresponding low

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