the $\bar{M}_n$ of the polymers increased with increasing conversion (Figure 5). The N values increased from ca. 0.5 to 1.0 as the polymerization proceeded (Figure 4b). The increase of polymer molecular weight with conversion shows that a long-lived propagating species is formed by iodine in toluene. However, this intermediate is not "living" in a strict sense, in view of the observed increase of N (Figure 4b), which is probably due to chain transfer occurring to some extent.

It is of interest that the polymerizations by iodine in toluene and in *n*-hexane differ considerably, though the solvents are both nonpolar. For instance, the N values for *n*-hexane (Figure 4c) do not exceed 0.5; those for toluene (Figure 4b) are already close to 0.5 at the beginning of the reaction and increase beyond this value with conversion. These facts indicate that initiation is faster in toluene than in *n*-hexane, whereas chain transfer is more frequent in the former solvent.

Although the polymerization by hydrogen iodide alone in *n*-hexane was very slow (Figure 1), in toluene this acid resulted in a rapid polymerization (ca. 100% conversion within 1 min), similar to that by HI/I_2. The MWD of the produced polymers was also similar to that with HI/I_2; no increase in polymer molecular weight with conversion was observed (Figure 8). Thus neither HI/I_2 nor HI alone could generate long-lived propagating species in toluene. Perhaps the π-electrons of this solvent may promote the ionic dissociation of the propagating species to give a less stable intermediate.

In conclusion, this work has shown that the HI/I_2 initiating system leads to an almost perfect living polymerization of IBVE in *n*-hexane, in which nearly monodisperse polymers are formed. To our knowledge, monodisperse polymers were obtained for the first time with an initiator for cationic polymerization. At present, the nature of the propagating species derived from the HI/I_2 system is unknown, and our current investigations concern this problem, which is important in understanding living cationic polymerization.

Registry No. Hydrogen iodide, 10034-85-2; iodine, 7553-56-2; poly(IBVE), 9003-44-5.

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Polyurethane Interpenetrating Polymer Networks (IPN's) Synthesized under High Pressure. 1. Morphology and T_g Behavior of Polyurethane–Poly(methyl methacrylate) IPN's

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ABSTRACT: A series of simultaneous interpenetrating polymer networks of polyurethane–poly(methyl methacrylate) were synthesized under high pressure (up to 20 000 kg/cm^2). The morphology via transmission electron microscopy and the glass transition behavior via DMA and DSC measurements were studied, and the effect of the synthesis pressure was evaluated. The composition of the polyurethane and poly(methyl methacrylate) was fixed at 50/50% by weight. The polyurethane phase domain sizes decreased from about 300 to 30 Å with increasing synthesis pressure from 1250 to 20 000 kg/cm^2. The phase continuity changed also with pressure; the polyurethane phase became continuous at low pressure, while the poly(methyl methacrylate) phase showed continuity at high pressure. A very broad glass transition ranging from about 0 to about 100 °C was observed for IPN's synthesized under 20 000 kg/cm^2, and they were optically transparent.

Introduction

The chemical and physical combination methods and their properties of multipolymers have been of commercial and academic interest, since it provides a convenient route for the modification of properties to meet specific needs. Among these methods, considerable interest has been given to interpenetrating polymer networks (IPN's).[1,2] IPN's are defined as a mixture of two or more cross-linked polymer networks which have partial or total physical interlocking between them. They have been prepared in three different modes of synthesis: latex blending,[3] sequential polymerization,[4,5] and simultaneous polymerization.[6-11] The degree of physical interlocking is dependent on the degree of phase separation at the time of interlocking (cross-linking in the presence of already cross-linked network). Thus by considering the mixture components of the three different synthetic methods, polymer–polymer mix in latex blending, polymer–monomer mix in sequential polymerization, and monomer–monomer (or oligomer–oligomer) mix in simultaneous polymerization, the simultaneous polymerization method would yield a higher degree of interpenetration.

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Like other multipolymer systems, incompatibility of IPN's arises from the usually low entropy of mixing obtained on blending the high molecular weight polymers. It is well understood that interpenetration plays a significant role in enhancing the compatibility of the polymer components due to the fact that the physical interlocking prohibits the phase separation from occurring when the molecular weight is built up to change the Gibbs free energy of the mixed system to be positive.[6] The cross-link density, the relative rate of network formation of each component, the rate of phase separation (dependent on medium viscosity, temperature, chain mobility, etc.), and the composition ratio all control the phase continuity and domain size.[12–14] The pressure can be another factor of enhancing the compatibility in multipolymer systems.

It has been observed that the compatibility increases with increasing pressure when the system has a negative volume change of mixing. Miyata[15] obtained a homogeneous blend of PVAc and PMMA at 10000 atm at 300 °C. The blend remained homogeneous when cooled to room temperature at atmospheric pressure, because both PVAc and PMMA were in a glassy state at room temperature thus the mobility of the polymer chain was not high enough to allow phase separation to occur. When the blend was thermally treated at 160 °C at atmospheric pressure, the two components separated into two phases. If we have interpenetration occurring under high pressure, for example, when carrying out simultaneous polymerization and cross-linking reactions while the mixture remains homogeneous, the physical interlocking will prevent the system from phase separation even if the mixture is brought to atmospheric pressure and thermally treated.

In this study, interpenetrating polymer networks (IPN's) of polyurethane (PU)–poly(methyl methacrylate) (PMMA) were prepared under varying pressures up to 20000 kg/cm^2 to study the effect of synthesis pressure on the compatibility. The morphology and glass transition behavior of the IPN's were analyzed to observe the degree of enhancement of compatibility with increasing synthesis pressure.

Experimental Section

Synthesis. The isocyanate-terminated polyurethane prepolymer was prepared by reacting 1 equiv of poly(tetramethylene ether) glycol (PTMG) with 2 equiv of MDI at 65 °C with 0.01 wt % of dibutyltin dilaurate. To a four-necked flask, equipped with a high-torque stirrer, thermometer, nitrogen inlet, and reflux condenser, was charged 2 equiv of MDI. It was heated to 65 °C, and the dibutyltin dilaurate (T-12) catalyst was injected. One equivalent of PTMG was slowly added with stirring. The reaction was carried out until the theoretical isocyanate content was reached as determined by the di-*n*-butylamine methods.

A mixture of 1,4-butanediol (1,4-BD) and trimethylolpropane (TMP) in 1:1 equiv ratio was used as the cross-linking and chain-extending agent for the PU network. Ethylene glycol dimethacrylate (EGDMA) was used as the cross-linking agent for the PMMA network. PU prepolymer, 1,4-BD/TMP mixture, MMA monomer, EGDMA, and benzoyl peroxide were mixed thoroughly, and the air entrapped during mixing was removed by applying a vacuum. This mixture was charged into a lead capsule (11 mm o.d., 9 mm i.d., 45 mm height), and this capsule was inserted into a cylindrical cavity of a mold made of SNCM 8 alloy steel (100 mm o.d., 11.5 mm i.d., 100 mm height). Pressure was applied through a piston rod in a 25 ton hydraulic press (Fred S. Carver Inc., Model-M 25 ton). The mixtures were simultaneously polymerized at 140 °C for 24 h with varying pressures from 0 to 20000 kg/cm^2. After the polymerization was completed, the mold was cooled to room temperature and the capsule was removed from the mold to take out the sample. The composition of the mixture was fixed at 50/50% PU/PMMA by weight. The theoretical number average molecular weight between cross-links ($\bar{M}_c$) was 3200 for each component. Samples were dried under vacuum at 50 °C for 2–3 days before testing.

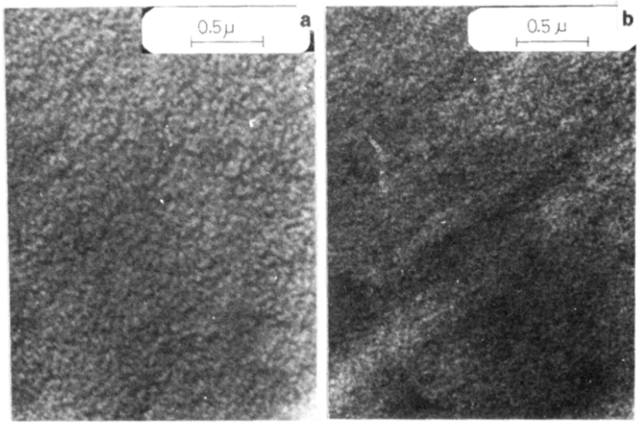

Figure 1. Electron micrographs of PU–PMMA (50/50) HPSIN synthesized at (a) 1250 kg/cm^2 and (b) 2500 kg/cm^2.

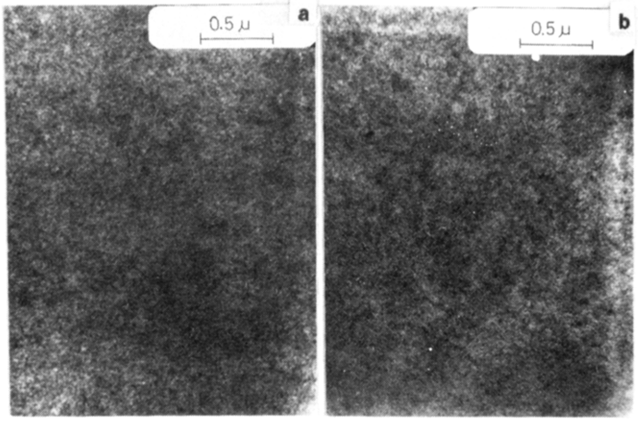

Figure 2. Electron micrographs of PU–PMMA (50/50) HPSIN synthesized at (a) 3750 kg/cm^2 and (b) 5000 kg/cm^2.

Electron Microscopy. Transmission electron micrographs were obtained on a JEM 100 CX (Jeol). The sample preparation technique used was based on Kato's osmium tetraoxide staining technique[16] and Matsuo's two-step sectioning method.[17]

Dynamic Mechanical Analysis (DMA). The dynamic mechanical properties were measured on a DuPont Model 981-990 dynamic mechanical analysis system. A constant heating rate of 10 °C/min was employed over a temperature range of −70 to 150 °C. The oscillation amplitude was 0.2 mm and gap setting was 13 mm. The DMA was a resonant frequency type, and the frequency range was 3–20 Hz. The test specimens were prepared in rectangular shape about 1.5 mm in thickness, 7 mm in width, and 24 mm in length.

Differential Scanning Calorimetry (DSC). The differential scanning calorimetry measurements were made on a DuPont Model 910 DSC and 990 thermal analyzer. The sample weight was about 10 mg, and the heating rate was 10 °C/min under nitrogen flow of 30 cm^3/min. Heating–quenching–heating cycles were employed, and the T_g was noted from the second heating thermograms from the midpoint of the transition.

Density. The density was measured by use of a density gradient column with sodium bromide aqueous solution as the medium.[18] All measurements were made at 24.5 °C. The experimental error was 4×10^{-4} g/cm^3, and the average of three measurements for each sample was taken.

Results and Discussion

Morphology. The morphology of the HPSIN (high-pressure simultaneous interpenetrating network) revealed fine dispersions of the component polymer domains, with sizes ranging from about 300 to 30 Å (Figures 1–4). The dispersed-domain sizes decreased as the synthesis pressure increased, and the samples were optically transparent when synthesized above 10000 kg/cm^2. Particularly, the HPSIN

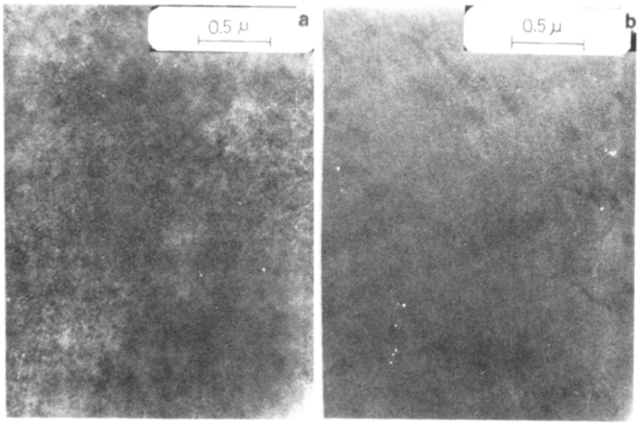

Figure 3. Electron micrographs of PU–PMMA (50/50) HPSIN synthesized at (a) 7500 kg/cm^2 and (b) 10 000 kg/cm^2.

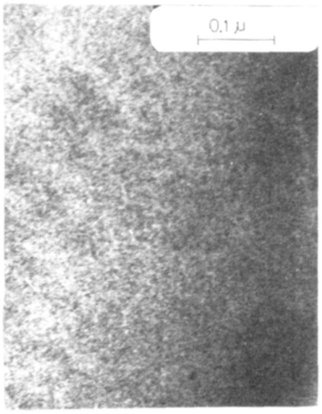

Figure 4. Electron micrograph of PU–PMMA (50/50) HPSIN synthesized at 20 000 kg/cm^2 (higher magnification).

synthesized at 20 000 kg/cm^2 pressure showed nearly molecular level mixing (Figure 4) with domain size of about 30 Å. The PU phase was stained by osmium tetraoxide and appears black and the unstained PMMA phase appears white in the micrograph.

SIN's with similar PU–PMMA composition but synthesized at atmospheric pressure showed heterogeneous morphology with large domain sizes ranging from 500 to 2000 Å.[7] The near molecular level of mixing in IPN could only be achieved previously with semicompatible polymer components (homologous polymer components such as poly(ethyl acrylate)–poly(methyl methacrylate)[5]) and had never been achieved before in incompatible IPN systems such as PU–PMMA SIN's. It is presumed that the simultaneously polymerizing mixture remained homogeneous due to the high external pressure and that the probability of forming a physical interlock is much higher when two polymers are simultaneously cross-linked with the close vicinity of the other component. This physical interlock will prohibit the phase separation from occurring when the pressure is removed. The role of high pressure in SIN synthesis is considered to be twofold; one is to enhance the compatibility of the polymerizing mixture (PU–PMMA IPN showed a negative volume change of mixing[8]), and the other is to raise the T_g of the polymers thus reducing the mobility of the chain for the phase separation.

The densities of the HPSIN's are shown in Figure 5. Although the data are scattered, they clearly show an abrupt increase in densities at synthesis pressure of 3000–5000 kg/cm^2. The calculated average of the two components is 1.145 g/cm^3, and the density increase is approximately 8.5 × 10^{-3} g/cm^3.

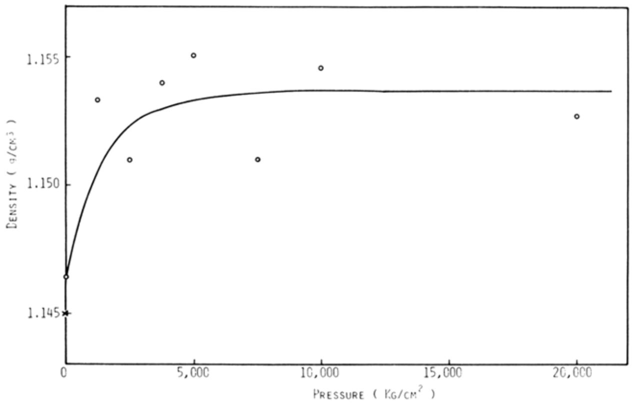

Figure 5. IPN density vs. synthesis pressure for PU–PMMA (50/50) HPSIN (x is the calculated density based on the volume additivity of the components).

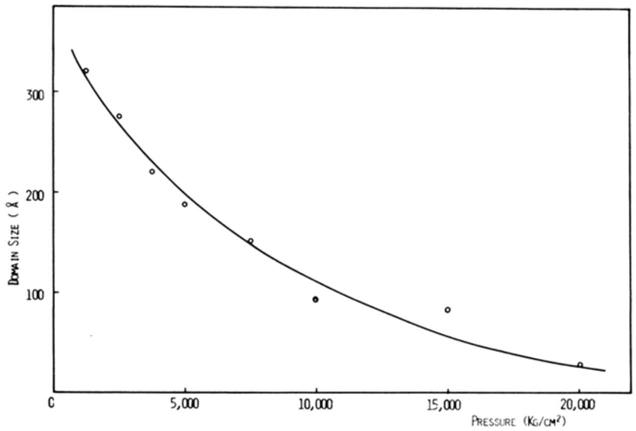

Figure 6. PU phase domain size vs. synthesis pressure for PU–PMMA (50/50) HPSIN's.

Table I
Glass Transition Temperature of PU–PMMA (50/50) HPSIN's

synthesis pressure, kg/cm^2	PU transition temp,[a] K		PMMA transition temp,[a] K	
	DSC	DMA	DSC	DMA
100	243	272	385	403
1250	243	271	387	401
2500	242	268	381	395
3750	243		377	388
5000			373	378
7500			374	
10000			370	
20000			368	368

[a] Pure-component T_g (synthesized at atmospheric pressure): PU (100), 245 K (DSC), 277 K (DMA); PMMA (100), 389 K (DSC), 415 K (DMA).

The domain sizes of the PU phase showed gradual decrease with increasing synthesis pressure from 300 Å at 1250 kg/cm^2 to 30 Å at 20 000 kg/cm^2 (Figure 6). At least 30 domains in each micrograph were measured by three different persons, and the average was calculated. The standard deviation was 30 Å when the average domain size was 300 Å, and it decreased gradually to 10 Å when the average domain size was 30 Å. The PU–PMMA (50/50) HPSIN's showed mostly cocontinuous morphology with the PU phase to be more continuous at low synthesis pressure and the PMMA phase to be more continuous at high pressure. This might be related to the change of the relative rate of formation of each component network with pressure.

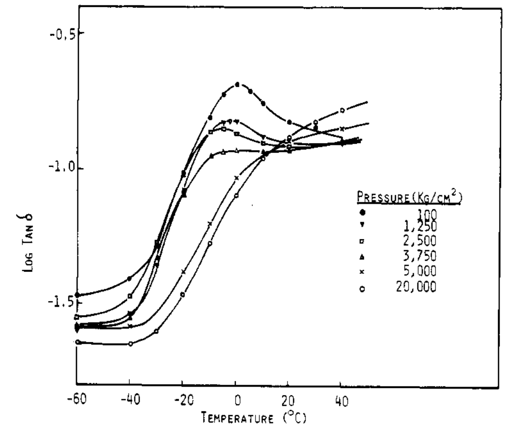

Figure 7. Effect of synthesis pressure on PU phase transition for PU–PMMA (50/50) HPSIN's.

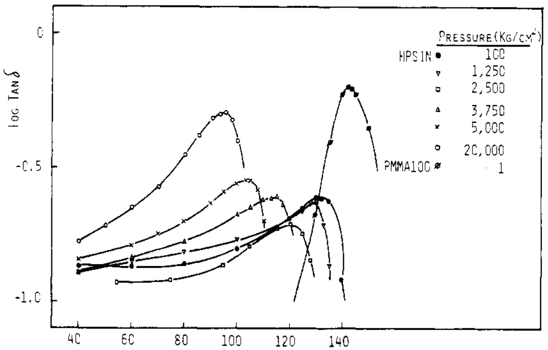

Figure 8. Effect of synthesis pressure on PMMA phase transition for PU–PMMA (50/50) HPSIN's.

Glass Transition Behavior. The glass transition temperatures of HPSIN's are listed in Table I. The peak temperature in the tan δ vs. temperature plot was taken as the T_g in the DMA measurement.

The PU transition of some samples was not detected because of difficulties in obtaining the midpoint in the DSC thermogram or the maximum peak point in the DMA curve when the sample showed a very broad transition. The PU–PMMA HPSIN's synthesized below 3750 kg/cm^2 exhibited two distinct but shifted T_g's corresponding to the respective component networks, and those synthesized above 5000 kg/cm^2 showed one broad T_g showing a shoulder of PU transition connected with PMMA transition. The height of the damping peak of the PU phase transition showed a gradual decrease with increasing synthesis pressure (Figure 7), while that of the PMMA phase, on the contrary, showed a gradual increase (Figure 8). This is related to the change of phase continuity observed in the morphology; the PU phase is more continuous at low pressure, and the PMMA phase is more continuous at high pressure. The PMMA T_g (peak point in tan δ vs. temperature plot) was gradually shifted toward low temperature with increasing synthesis pressure as the degree of intermixing with the PU phase increased, as evidenced by the decrease in domain size in the morphology. The maximum shift of the PMMA T_g was 47 °C in the DMA measurement and was 21 °C in the DSC measurement at 20 000 kg/cm^2 synthesis pressure. The PMMA T_g shift as observed by DMA is shown in Figure 9. If the degree of shift is considered to be due to the intermixing of the PU in the PMMA domain and if we assume that the simple Fox equation is valid in this mixture, the T_g shift at 20 000 kg/cm^2 corresponds to the intermixing of 24% PU and 76% PMMA by weight in the PMMA domain. The Young's modulus vs. temperature plot (Figure 10) showed two distinct T_g's in HPSIN's synthesized under low pressure (0–3750 kg/cm^2) and one broad transition in HPSIN's synthesized under high pressure (20 000 kg/cm^2), which also showed the increased degree of interpenetration of the component networks when SIN was synthesized at high pressure.

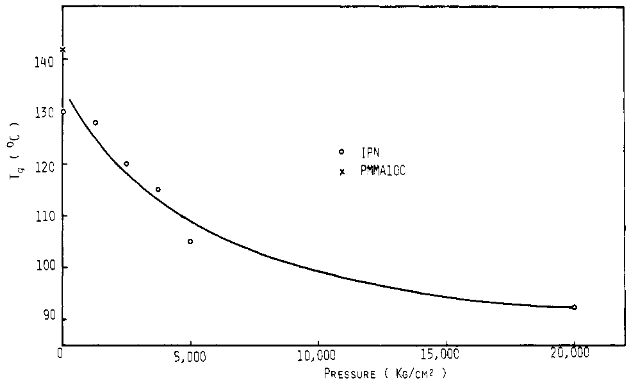

Figure 9. Effect of synthesis pressure on the PMMA T_g measured by DMA for PU–PMMA (50/50) HPSIN's.

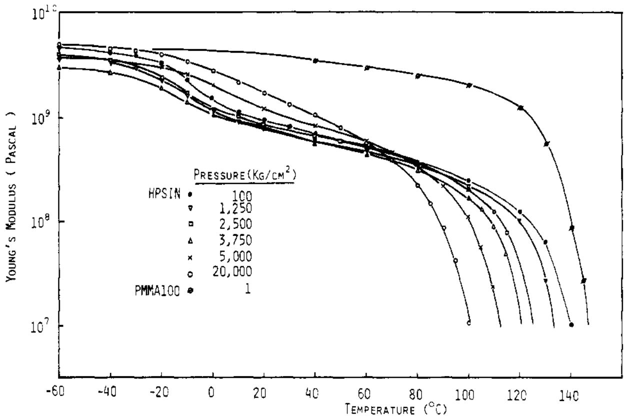

Figure 10. Young's modulus vs. temperature for PU–PMMA (50/50) HPSIN's.

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Registry No. (MMA)·(EGDMA) (copolymer), 25777-71-3; (PTMG)·(MDI)·(1,4-BD)·(TMP) (polymer), 39281-41-9.

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Some Chemical and Analytical Aspects of Polysaccharide Modifications.[1] 3. Formation of Branched-Chain, Soluble Chitosan Derivatives[2]

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ABSTRACT: Specific attachment of carbohydrates to the 2-amino functions of chitosan transforms this water-insoluble, linear polymer into branched-chain water-soluble derivatives. Facile conversions can be achieved by reductive alkylation using sodium cyanoborohydride and any aldehydo or keto sugar, by Schiff base formation, or by amidation reactions using carboxylic acid or lactone derivatives. Experimental results are presented for a series of mono-, di-, tri-, and polysaccharides, including D-glucose, *N*-acetylglucosamine, D-glucosamine, D-galactose, D-galactosamine, D-fructose, D-glucoheptonic acid γ-lactone, lactose, cellobiose, maltose, melibiose, maltotriose, streptomycin sulfate, C^6-*aldehydo*-cycloheptamylose, and dextran. These procedures facilitate the preparation of polymer derivatives with a variety of comblike, treelike, and other branching types. Many of these products are amenable to further, specific chemical modifications; this is demonstrated by the introduction, via galactose oxidase treatment, of C-6 aldehyde functions into the pendant galactose residues of derivatives **8** and **13**. The synthetic chitosan derivatives exhibit a number of useful and uncommon properties in terms of their solution characteristics. Thus, aqueous solutions of derivative **8** were compatible with a wide range of salts, and derivatives **11** and **13** were stable in 50% aqueous ethanol. Derivative **8** formed inclusion complexes with iodine, lactose, and 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl. Solubility modifications were accomplished by coreaction of hydrophilic (lactose) and hydrophobic (various alkyl) residues, affording products, such as **24**, which were soluble in both aqueous and organic media. Reductive alkylation of chitin afforded the 1-deoxylactit-1-yl derivative **27**, which was water insoluble but formed sols in water and several organic solvents. Factors affecting the solution behavior of chitosan and its branched derivatives have been evaluated and mechanisms have been discussed for solute interactions and conformational transitions.

Introduction

In contrast to most other polysaccharides, both chitin, a β(1-4)-linked 2-deoxy-2-acetamido-D-glucopyranosyl polymer, and chitosan, its *N*-deacetylated derivative, exhibit basic properties (pK_a of chitosan is 6.3) which impart them with unique characteristics in terms of solution properties, membrane-forming ability, and metal chelation capacity.[4] Chitin is widely distributed in nature with an estimated[5] annual natural production of 10^{10}–10^{11} tons, yet this inexpensive biopolymer has attracted, by comparison with for example cellulose, relatively little attention mainly as a result of its intractability. Thus, both chitin and chitosan are insoluble in common organic solvents, water, dilute acids, or cold alkalis of any concentration. Only a few solvent systems reportedly do not give rise to hydrolysis of the amide or glycosidic linkages;[4] these include hexafluoro-2-propanol, hexafluoroacetone sesquihydrate, certain chloro alcohols, and lithium chloride in *N*,*N*-dimethylacetamide solutions for chitin[6] and a number of organic acids, such as acetic and formic acid, for chitosan. Clearly, these solvents offer only very limited utility for chemical derivatizations in homogeneous solution, particularly for large-scale applications.

In this study we report the use of reductive alkylation as a facile and versatile procedure for covalent attachment of a diverse range of carbohydrates and other substrates to the primary amine functions of chitin and chitosan. As part of a general program of selective chemical modifications of polysaccharides, this work pursued two major interests. Our first objective was to develop derivatization methods which could ultimately lead to a greater commercial utilization of chitin and chitosan. The second, conceptually more challenging goal involved the synthesis of model compounds which would facilitate systematic investigations of the structure/function relationship of polysaccharides. Although some of the properties of polysaccharides are known to follow certain trends, a methodical understanding of the relation of their primary structure to their aqueous solution characteristics and solute interactions, etc., remains to be established.[5,7]

Clearly, one of the keys to any successful large-scale utilization of chitin/chitosan lies in the resolution of the intractability of these polymers. It would be desirable to design versatile synthetic routes for the formation of water- or organic-soluble products or, ideally, of derivatives whose solubility and hydrophobicity could be tailored. Previous specific derivatizations of the primary amine group of chitosan[8] have invariably afforded insoluble products. Although certain water soluble ether and salt derivatives of chitosan are known,[4] there have been no efforts to affect solubilization by introducing suitable hydrophilic moieties onto the polymer backbone. Similarly, there are only a few examples of derivatized chitins and chitosans which are soluble in organic solvents;[6,9] none of the reported derivatives is soluble in both organic and aqueous solvents. As we shall demonstrate, the methods described here allow the preparation of chitosan derivatives which are of the latter type.

Prerequisite to any systematic investigations of the structure/function relationship of polysaccharides is the availability of versatile strategies which would allow the synthesis of branched polymers, whose branch type, branch

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