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Living Cationic Polymerization of *N*-Vinylcarbazole Initiated by Hydrogen Iodide

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ABSTRACT: Living cationic polymerization of *N*-vinylcarbazole (NVC) was achieved with hydrogen iodide (HI) as an initiator either at -40°C in toluene or at -78°C in methylene chloride containing a catalytic amount of tetra-*n*-butylammonium iodide as a common ion salt. The number-average molecular weight of the polymers obtained under these conditions was directly proportional to NVC conversion or to the NVC/HI feed ratio and in good agreement with the calculated values assuming that one HI molecule forms one living chain. The polymers exhibited a narrow molecular weight distribution with a \bar{M}_w/\bar{M}_n ratio from 1.2 to 1.3. The corresponding polymerizations by iodine or a mixture of HI and iodine (HI/I_2 initiator) were not living, yielding polymers with a broader molecular weight distribution. The scope of living cationic polymerization is also discussed in terms of the stability of the propagating carbocation and the nucleophilicity of the counteranion.

Introduction

N-Vinylcarbazole (NVC) is among the most reactive vinyl monomers in cationic polymerization. Its high cationic polymerizability arises from the electron-donating carbazolyl pendant, which also serves to stabilize the propagating NVC cation by providing a conjugating system where the positive charge is delocalized.

In view of the stability of the NVC-derived growing species, we have been interested in "living" cationic polymerization of this monomer^{1,2} and in fact found that the NVC polymerization initiated by iodine yields living polymers with a controlled molecular weight and a narrow molecular weight distribution (MWD).² This living system is, however, operative only in a limited range of reaction conditions, i.e., at -78°C in methylene chloride containing tetra-*n*-butylammonium iodide (*n*-Bu₄NI) as a common ion salt.

More recent investigations in our laboratories have provided a number of living cationic polymerizations initiated by a mixture of hydrogen iodide (HI) and iodine.^{3,4} Although efficient and versatile, the HI/I_2 initiating system has thus far been applied to only vinyl ethers⁴ and related monomers.⁵ Another characteristic of the binary system is that both HI and iodine are indispensable for living polymerization; HI alone cannot polymerize vinyl ethers but forms a 1:1 adduct $[\text{CH}_3\text{CH}(\text{OR})-\text{I}]$, the C-I bond of which must be activated by iodine to initiate living propagation.⁶ Namely, HI is the initiator, while iodine acts as the "activator".

The primary object of this study was to extend the scope of the HI/I_2 -initiated living polymerization to NVC, a reactive monomer other than vinyl ethers and their analogues. Rather surprisingly, not HI/I_2 but HI alone was

found to initiate living polymerization of NVC under conditions wider than those for the corresponding process with iodine. This new combination of monomer and initiator enables us to discuss the scope of living cationic polymerization in terms of the stability of the propagating species (carbocations) and the nucleophilicity of the counteranions derived from initiators.

Experimental Section

Materials. Commercial NVC was recrystallized at least 3 times from *n*-hexane, thoroughly dried in vacuo, and stored in the dark at -20°C . HI (as an *n*-hexane solution) and iodine were obtained as reported.³ *n*-Bu₄NI (polarographic grade) was used as received after prolonged vacuum drying. Polymerization solvents [toluene and methylene chloride (CH_2Cl_2)] and the internal standard for gas chromatography (tetrahydronaphthalene) were purified by the usual methods³ and doubly distilled over calcium hydride before use.

Procedures. Polymerization was carried out in the dark under dry nitrogen in a baked glass tube equipped with a three-way stopcock.³ The reaction was initiated by injecting an initiator solution via a dry syringe into a monomer solution and terminated after a certain period with prechilled ammoniacal methanol. When the HI/I_2 initiator was employed, HI and iodine solutions were added successively in this order. The NVC conversion was determined by gas chromatography with tetrahydronaphthalene as an internal standard. The quenched reaction mixture was washed sequentially with 10% aqueous sodium thiosulfate solution and with water, evaporated to dryness under reduced pressure, and vacuum dried to give the product polymers.

The MWD of the polymers was measured by size-exclusion chromatography (SEC) in chloroform at room temperature on a Jasco Trirotar-II instrument equipped with three polystyrene gel columns (Shodex A-802, A-803, and A-804). The polydispersity ratio (\bar{M}_w/\bar{M}_n) was calculated from the SEC curves on the basis of a polystyrene calibration. The number-average molecular

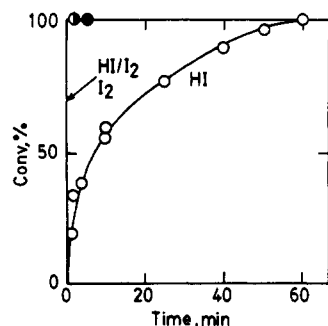


Figure 1. Time-conversion curves for the polymerizations of NVC in toluene at $-40\text{ }^{\circ}\text{C}$ and $[\text{NVC}]_0 = 0.20\text{ M}$. Initiators (mM): (○) HI (2.0); (●) iodine (2.0); (○) HI/ I_2 (2.0/2.0).

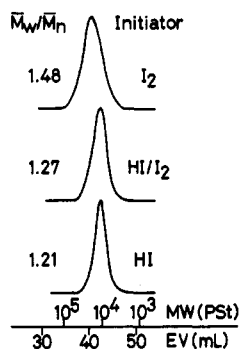


Figure 2. MWD of poly(NVC) obtained with the indicated initiators at 100% conversion; see Figure 1 for reaction conditions.

weight (\bar{M}_n) of the polymers was determined both by vapor pressure osmometry (VPO) (Knauer Model No. 11.00, in toluene at $-37\text{ }^{\circ}\text{C}$) and by SEC (polystyrene calibration). Under our analysis conditions, the \bar{M}_n values by the two methods were proportional to each other [$\bar{M}_n(\text{VPO}) = 1.55\bar{M}_n(\text{SEC})$ for $\bar{M}_n(\text{SEC}) < 3 \times 10^4$]; therefore, most of the \bar{M}_n values reported in this paper were conveniently obtained by SEC and then converted into the VPO values by using this relationship.

Results and Discussion

1. Polymerization by HI/ I_2 and HI: Effects of Initiators. NVC was polymerized by HI/ I_2 and HI alone in toluene at $-40\text{ }^{\circ}\text{C}$. Iodine was also employed as an initiator^{1,2} for comparison. Since NVC monomer is sparingly soluble in nonpolar solvents at low temperature, its initial concentration was kept rather low ($[\text{NVC}]_0 = 0.20\text{ M}$).

Figure 1 compares the time-conversion curves for the polymerizations by the three initiators. HI/ I_2 and iodine induced very rapid reactions that reached 100% conversion within 2–3 min. A much slower but quantitative polymerization occurred with HI alone; it involved no induction phase and was completed in 1 h. In all these polymerizations, the initially homogeneous reaction mixture turned cloudy above 30% NVC conversion, with white fine powder of poly(NVC) suspended in the solution. It is important that NVC can be polymerized by HI alone, which is incapable of initiating polymerization of vinyl ethers under similar conditions (in toluene below $-15\text{ }^{\circ}\text{C}$).^{3,4}

Figure 2 illustrates the MWDs of the polymers thus obtained with the three initiators at 100% conversion. They are all narrow ($\bar{M}_w/\bar{M}_n = 1.2\text{--}1.5$); interestingly, HI led to the narrowest. These results show that not only is iodine^{1,2} but also HI and HI/ I_2 are promising as initiators for living polymerization of NVC.

2. Living Polymerization of NVC by HI Alone. **Polymerization in Toluene.** Noting the narrow MWD of the polymers obtained with HI alone, we then studied more in detail the possibility of living polymerization of

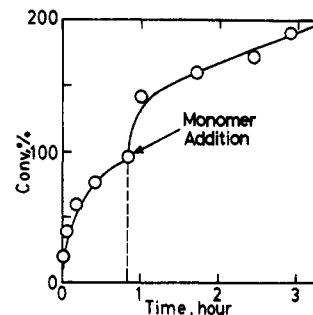


Figure 3. Time-conversion curve for a monomer-addition experiment in the NVC polymerization by HI in toluene at $-40\text{ }^{\circ}\text{C}$: $[\text{NVC}]_0 = 0.20\text{ M}$; $[\text{HI}]_0 = 2.0\text{ mM}$. The molar amount of NVC in the second feed is the same as in the first.

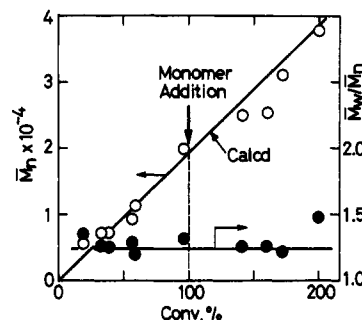


Figure 4. \bar{M}_n and \bar{M}_w/\bar{M}_n values of poly(NVC) obtained before and after the monomer addition in the polymerization by HI in toluene at $-40\text{ }^{\circ}\text{C}$, as a function of NVC conversion; see Figure 3 for reaction conditions. The diagonal line indicates the \bar{M}_n values calculated with the assumption that one HI molecule forms one living chain.

NVC by this protonic acid. The most important characteristic of living polymers is their ability to resume propagation on addition of a fresh feed of monomer even after the previous feed has been completely depleted; their molecular weight (\bar{M}_n) increases in direct proportion to monomer conversion both before and after the monomer addition. Figures 3 and 4 give the results of such "monomer-addition" experiments for the polymerization of NVC by HI in toluene at $-40\text{ }^{\circ}\text{C}$.

Thus, when the first-stage polymerization was completed in 1 h (cf. Figure 1), a fresh feed of NVC in toluene, in the same molar amount as in the first feed, was added to the reaction mixture. A second-stage polymerization immediately ensued without an induction phase and reached a quantitative conversion in ca. 2 h (Figure 3). The initial rate of the second stage was nearly half that of the first, because the volume of the reaction mixture was doubled by the addition of the NVC solution. Even when the second NVC feed was supplied 2 h after the end of the first-stage reaction, a smooth polymerization occurred at nearly the same rate.

Figure 4 plots the \bar{M}_n and \bar{M}_w/\bar{M}_n values of the polymers, obtained before and after the monomer addition, as a function of NVC conversion. The polymer molecular weight was directly proportional to conversion, and its linear increase continued even after the addition of NVC. Throughout these experiments, the MWD of the polymers remained narrow ($\bar{M}_w/\bar{M}_n = 1.2\text{--}1.3$). The observed \bar{M}_n s were in good agreement with the calculated values with the assumption that one HI molecule forms one polymer chain (the straight line in Figure 4).

Separate experiments showed that the polymer molecular weight can also be controlled by simply regulating the feed ratio of NVC to HI (Figure 5), which is another feature of living processes. In these experiments, the initial

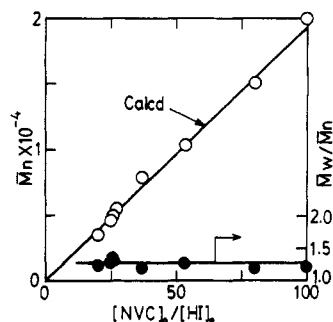


Figure 5. \bar{M}_n and \bar{M}_w/\bar{M}_n values for poly(NVC) obtained in the polymerization by HI in toluene at -40°C , as a function of the monomer-to-initiator feed ratio: $[\text{NVC}]_0 = 0.20\text{ M}$; conversion = 100%. The diagonal line indicates the \bar{M}_n values calculated with the assumption that one HI molecule forms one living chain.

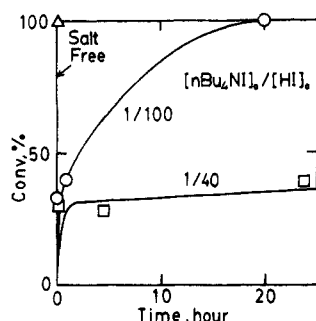


Figure 6. Effect of a common ion salt ($n\text{-Bu}_4\text{NI}$) on the NVC polymerization by HI in CH_2Cl_2 at -78°C : $[\text{NVC}]_0 = 0.20\text{ M}$; $[\text{HI}]_0 = 4.0\text{ mM}$. $[n\text{-Bu}_4\text{NI}]_0/[\text{HI}]_0$: (Δ) 0 (salt free); (\circ) 1/100; (\square) 1/40.

HI concentration ($[\text{HI}]_0$) was varied, while the initial monomer concentration ($[\text{NVC}]_0$) was kept constant. The molecular weight of the polymers obtained at 100% conversion was directly proportional to the NVC/HI feed ratio and in good agreement with the calculated values (see above). All these polymers exhibited a narrow MWD (Figure 5), independent of the monomer-to-initiator feed ratio.

NVC could also be polymerized by HI alone in toluene at a lower temperature (-78°C) ($[\text{NVC}]_0 = 0.20\text{ M}$, $[\text{HI}]_0 = 2.0\text{ mM}$). However, the polymerization stopped at ca. 60% conversion in 2 h, and little increase in conversion was observed on prolonged standing of the reaction mixture for up to 10 h. The MWD of the produced polymers was broader than those for -40°C ; e.g., $\bar{M}_w/\bar{M}_n = 1.39$ (-78°C) vs. 1.19 (-40°C), conversion ca. 60%. Thus, the polymerization at -78°C is not living.

The results summarized in Figures 3–5 demonstrate the living nature of the NVC polymerization by HI in toluene at -40°C .

Polymerization in Methylene Chloride: Effects of Solvent Polarity and Common Ion Salt. Although the NVC polymerization by HI in toluene at -40°C is living, the reaction mixture is heterogeneous above 30% NVC conversion, and the MWD of the resultant polymers was broader than those of living poly(vinyl ethers) obtained by HI/I_2 .^{3,4} We thus carried out polymerization of NVC by HI in CH_2Cl_2 , which is more polar than toluene and would give a homogeneous system even at low temperature. Preliminary experiments soon revealed that the polymerization at -40°C in this solvent, though homogeneous as expected, is too fast (completed within 30 s) to be adequately controlled and eventually gives nonliving polymers with a broad MWD ($\bar{M}_w/\bar{M}_n = 1.7\text{--}1.8$). The temperature was therefore lowered to -78°C .

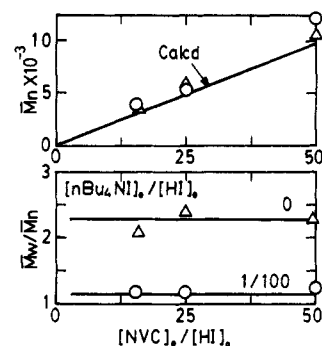


Figure 7. \bar{M}_n and \bar{M}_w/\bar{M}_n values of poly(NVC) obtained in the polymerization by HI in CH_2Cl_2 at -78°C , as a function of the monomer-to-initiator feed ratio: $[\text{NVC}]_0 = 0.20\text{ M}$; conversion = 100%. $[n\text{-Bu}_4\text{NI}]_0/[\text{HI}]_0$: (Δ) 0 (salt free); (\circ) 1/100. The solid line in the \bar{M}_n -conversion plots indicates the \bar{M}_n values calculated with the assumption that one HI molecule forms one living chain.

Figure 6 shows the time-conversion profiles for the HI-initiated polymerization in CH_2Cl_2 at -78°C in the presence and absence of $n\text{-Bu}_4\text{NI}$, a common ion salt that suppresses the ionic dissociation of the propagating species in polar media.^{4a} The polymerization in salt-free CH_2Cl_2 was still so rapid as to be completed in 1 min. Addition of $n\text{-Bu}_4\text{NI}$ remarkably retarded the reaction; it took 20 min to obtain a quantitative conversion of NVC at the salt/HI mole ratio = 1/100, whereas the conversion apparently leveled off at ca. 30% at a higher salt concentration (salt/HI = 1/40). In all cases, the polymerization solutions stayed homogeneous up to 100% NVC conversion.

The living nature of the polymerizations at -78°C was then examined by plotting the \bar{M}_n and \bar{M}_w/\bar{M}_n values of the obtained polymers as a function of the $[\text{NVC}]_0/[\text{HI}]_0$ feed ratio (Figure 7). Both in the absence and presence of the common ion salt (salt/HI = 1/100), the polymer molecular weight is directly proportional to the monomer-to-initiator feed ratio and in good agreement with the calculated values for living polymers (one polymer chain per one HI molecule).

The common ion salt, however, affected the MWD of the polymers, as also shown in Figure 7. The poly(NVC) produced in salt-free CH_2Cl_2 exhibited a broad MWD with a \bar{M}_w/\bar{M}_n ratio greater than 2. In contrast, quite narrow distributions ($\bar{M}_w/\bar{M}_n = 1.18\text{--}1.26$), even narrower than those with toluene (Figures 4 and 5), were obtained in the polymerization in the presence of $n\text{-Bu}_4\text{NI}$. This indicates that a better living system has been obtained in CH_2Cl_2 where the homogeneity of the reaction solution can be maintained.

In the absence of the salt, the propagating species is dissociated and reactive, because of the polarity of CH_2Cl_2 , and it induces a rapid polymerization where the initiation is slower than the propagation. Thus a broad MWD results, though the lifetime of the intermediate is long enough to maintain the linear increase in polymer molecular weight with $[\text{NVC}]_0/[\text{HI}]_0$. In contrast, the added common ion salt suppresses the dissociation of the growing end, in turn renders the propagation slower than the initiation, and then gives the narrow MWD of the polymers. Thus, the NVC polymerization by HI at -78°C in salt-containing CH_2Cl_2 is living, similarly to that in toluene at -40°C .

3. Polymerization by HI/ I_2 Initiator. The polymerization of NVC was also carried out by using this binary initiating system to compare its characteristics with those initiated by HI alone. Figure 8 shows the molecular weight

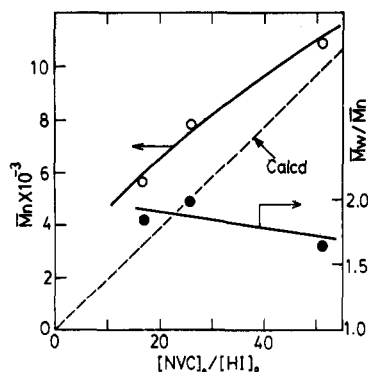


Figure 8. \bar{M}_n and \bar{M}_w/\bar{M}_n values of poly(NVC) obtained in the polymerization by HI/I₂ in toluene at -40 °C, as a function of the monomer-to-initiator feed ratio: $[NVC]_0 = 0.20$ M; $[HI]_0/[I_2]_0 = 4.0$; conversion = 100%. The broken line indicates the \bar{M}_n values calculated with the assumption that one HI molecule forms one living chain.

and MWD of the polymers thus prepared in toluene at -40 °C, as a function of the monomer-to-initiator feed ratio. As already described (Figures 1 and 2), the polymerization was very fast, and the polymers exhibited a broad MWD ($\bar{M}_w/\bar{M}_n = 1.6$ –2.0). When the initial HI concentration was varied while that of NVC was kept constant, the polymer molecular weight indeed increased with increasing $[NVC]_0/[HI]_0$ ratio but was not proportional to it. In addition, the observed \bar{M}_n s are larger than the calculated values for living polymers. Similar overall results were also obtained for the HI/I₂-initiated polymerizations at -78 °C in CH₂Cl₂, both in the presence and absence of *n*-Bu₄NI. These facts show that HI/I₂ cannot induce living polymerization of NVC under all conditions examined in this study.

The very high rate of the polymerization by HI/I₂ (Figure 1) indicates the involvement of a growing species which is more reactive than that generated by HI alone, because its active end is most likely activated by iodine.⁶ The high polymerization rate may lead to the polymer molecular weight higher than the calculated value based on the monomer-to-initiator feed ratio; the propagation is so fast that all the NVC feed is completely polymerized before the initiation is completed. Another disadvantage of the HI/I₂ system is that not only HI but also iodine can initiate polymerization of NVC (cf. Figure 1). Such a simultaneous and parallel initiation by both initiator components may also account for the broad MWD of the polymers.

4. Scope of Living Cationic Polymerization. The most important finding of this study is that HI alone can induce living polymerization of NVC. The NVC/HI system is unique in that this acid by itself cannot polymerize vinyl ethers and requires the presence of iodine as the activator (see Introduction) for their living polymerization.^{4,6} Thus, we now have three major monomer/initiator combinations for living cationic processes: (A) NVC–HI; (B) vinyl ethers–HI/I₂³ and *p*-methoxystyrene–HI/I₂;⁷ (C) *p*-methylstyrene–acetyl perchlorate.⁸

According to our principle of living cationic polymerization,^{4a} a suitably strong interaction between the growing carbocation and its counteranion is critically important to suppress chain transfer and termination.⁹ Such an interaction in the propagating species is affected by two internal factors: the stability of the growing carbocation derived from a monomer and the nucleophilicity of the counteranion derived from an initiator. The above three monomer/initiator combinations differ considerably in these two factors, and their differences in turn give us a

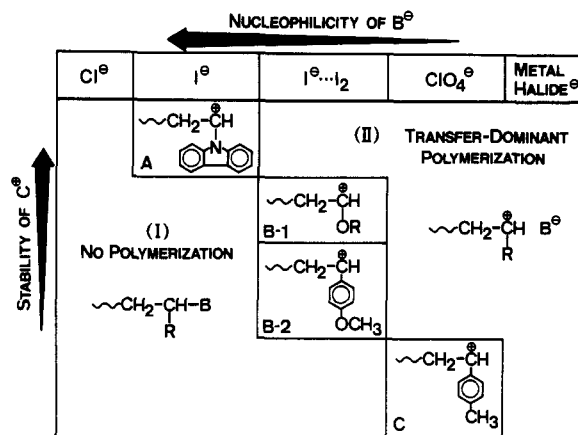


Figure 9. Scope of living cationic polymerization of vinyl monomers. Boxes A, B-1, B-2, and C indicate the monomer/initiator combinations for living polymerization.

perspective to discuss the scope of living cationic polymerization.¹⁰

In Figure 9, therefore, the typical monomer/initiator combinations for cationic polymerizations are summarized in terms of the stability of growing carbocations and the nucleophilicity of counteranions; the four boxes (A, B-1, B-2, and C) indicate the combinations for living polymerization.

For vinyl ethers and *p*-methoxystyrene, which form moderately stable carbocations, HI cannot initiate their polymerization because the iodide anion is so nucleophilic and interacts so strongly with the cations that it undergoes termination by forming a terminal carbon-iodine linkage (region I, Figure 9). In order to induce propagation, the carbon-halogen bond must be externally activated by an electrophile like iodine,⁶ and this is exactly the case for the living polymerization of vinyl ethers and *p*-methoxystyrene by the HI/I₂ initiating system (boxes B-1 and B-2). When a less nucleophilic counteranion (e.g., the perchlorate anion) is employed, the cation-anion interaction at the active end is too weak to suppress side reactions, so that a non-living, transfer-dominant polymerization occurs (region II).

For NVC, which forms a more stable carbocation than vinyl ethers do, the nucleophilic iodide anion now does not undergo termination but maintains a suitably strong interaction with the NVC cation and thereby leads to living propagation; no assistance of iodine as an activator is necessary, as shown in this study (box A). At another end of the spectrum lies the *p*-methylstyrene/acetyl perchlorate system (box C), in which the growing carbocation is less stable and requires a less nucleophilic perchlorate counteranion to undergo living polymerization. Note that *p*-methylstyrene can be polymerized neither by HI/I₂ nor by HI alone (region I).

The above discussion suggests that new living polymerization systems can be designed by selecting suitable combinations of monomer (carbocation) and initiator (counteranion).

Registry No. NVC, 1484-13-5; NVC (homopolymer), 25067-59-8; *n*-Bu₄NI, 311-28-4; HI, 10034-85-2; I₂, 7553-56-2.

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Synthesis and Characterization of Vesicles Stabilized by Polymerization of Isocyano Functions

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ABSTRACT: Coupling of dimethylhexadecyl(11-hydroxyundecyl)ammonium bromide with the *N*-formyl derivatives of L-alanine and L-valine and dehydration of the reaction products with phosphorus oxychloride and base yield the double-chain quaternary ammonium surfactants 1 and 2, respectively. Via a similar sequence of reactions, starting from (*N*-formylamino)caproic acid and dimethyleicosyl- and dimethyldocosyl(11-hydroxyundecyl)ammonium bromide, the surfactants 3 and 4 are obtained. Amphiphiles 1-4 contain polymerizable isocyano functions located at different positions along the hydrocarbon chains. On dispersing in water these compounds form vesicles. Freeze-fracture electron microscopy and osmotic experiments indicate that the structures of the aggregates are closed. According to differential scanning calorimetry measurements the vesicles undergo a phase transition in the temperature range of -3 to -22 °C. Addition of nickel capronate to the vesicle dispersions results in polymerization of the isocyano functions in the bilayers. This polymerization proceeds more effectively for the isocyano functions at the end of the hydrocarbon chains than for the isocyano functions located in the middle section. The molecular weights vary between ~8000 and 45 000. Electron micrographs indicate that in vesicles of 3 and 4 the polymerization process is restricted to each of the monolayers. In 1 and 2 this process also includes the bilayer. Osmotic experiments and electron micrographs indicate that on polymerization the structure of the vesicles is retained, but the phase transitions disappear. Fluorescence experiments with the probes 8-anilino-1-naphthalenesulfonate and *N*-phenyl-1-naphthylamine reveal that the bilayers of the polymerized vesicles are less polar than those of the unpolymerized ones. This is the case for both the head-group region and the core of the bilayer matrix. From fluorescence isotope experiments in water and in D₂O we infer that in the polymerized vesicles the lower polarity of the head-group region is due to the extrusion of water molecules. The lower polarity of the core is probably correlated to the disappearance of the isocyano functions. Fluorescence experiments with the viscosity probe pyrene and fluorescence depolarization experiments with the probe 1,6-diphenyl-1,3,5-hexatriene suggest that on polymerization the bilayers of the vesicles become more viscous. On going from 1 to 4 the difference in fluorescence anisotropy values between polymerized and unpolymerized vesicles becomes smaller. This trend in declining difference of anisotropy values parallels the trend of decreasing molecular weight in polymerized 1-4. For comparison fluorescence data are also included of experiments with vesicle systems prepared from dihexadecyldimethylammonium bromide, dioctadecyldimethylammonium bromide, egg yolk lecithin, dipalmitoylphosphatidylcholine, and a polymerizable methacrylate amphiphile.

Introduction

Phospholipids and double-chain synthetic surfactants form closed bilayer structures in water, known as liposomes and surfactant vesicles, respectively.¹ Because of their structural similarity to biological membranes, these aggregates are now widely being used in membrane mimetic studies.² In addition, these systems are of current interest as they could be applicable as devices for photochemical energy conversion,³ slow release of drugs,⁴ and as microreactors.⁵ A drawback of liposomes and surfactant vesicles, however, is their limited stability, which obstructs their use in practical applications. In order to overcome this problem, several research groups have recently prepared polymerized vesicles from amphiphiles that contain diacetylene, butadiene, methacrylate, styrene, vinyl, thiol, amino acid, and isocyano groups.⁶ A prerequisite for the exploitation of these systems is a good characterization of

the structure of the polymerized aggregates. Detailed information can be obtained by applying the fluorescent probe technique. This technique has already been proved useful in studies of the structure and function of biological membranes *in vivo*.⁷ Compared to other methods, such as EPR and NMR, the advantages are high sensitivity, low degree of membrane perturbation, and primary response to the environment.^{7,8} The fluorescent probe technique has also been applied for the characterization of liposomes, enzymes, micellar systems,⁹ and, more recently, synthetic surfactant vesicles.⁹ Only a few reports deal with polymerized vesicle systems. Nome et al. studied the influence of vesicle polymerization on the fluorescence of pyranine.¹⁰ They found that polymerization induces the formation of clefts on the vesicle surface.

In this paper, we describe the synthesis and characterization by fluorescence methods of unpolymerized and