NOTE

DNA/Lipid Complex Organogel with Shape-Memory Behavior

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ABSTRACT: DNA and amphiphilic *N,N,N*-trimethyl-*N*-hexadecylammonium bromide (THAB) were stoichiometrically mixed together to produce a DNA–lipid complex, which was dissolved in dimethyl sulfoxide (DMSO) at 65°C and then crosslinked with isophorone diisocyanate (IPDI). The obtained organogel swelled reversibly in DMSO, responding to the variation of temperature. Interestingly, we observed that the gel exhibited a temperature-dependent shape-memory behavior. Above 65°C, whatever the shape the gel was deformed to, it could retain the new shape as the temperature was decreased to room temperature, while, when the gel was heated to 65°C again, it could recover its initial shape. The shape-memory characteristic is supposedly originated from the transition between the close-packed and the destroyed DNA/lipid conformation. The elastic urethane crosslinking bonds between base-pair sites act as a fixing phase. The gel holds promise in its application as a gentle actuator. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 259–263, 2002

INTRODUCTION

During the past decade, stimuli-responsive polymer gels, which are capable of adjusting their volume or shape in response to the surrounding media (pH,[1] temperature,[2] electrical field,[3] and chemical composition[4]), have aroused worldwide research attention due to their great potential applications as "smart materials," including in controlled drug-delivery systems,[5] culture substrates,[6] chemical valves,[7] and gentle actuators.[8] The polymer-constructing gels have been extended from synthetic species to biological origins such as polysaccharide and protein.[9–13] Few studies, however, have been carried out on the construction of a gel from deoxyribonucleic acid (DNA).[14] Besides its genetic significance, DNA is also a naturally occurring macromolecule with specific selectivity and delicate molecular recognition.[15] In addition, its phosphate groups on the backbone and amino moieties on the base pairs are potential reactive sites. Creating a functional or structural material using DNA as a building block will undoubtedly open up a new avenue for material synthesis beyond a mere academic curiosity level. Here, we report on a temperature-dependent shape-memory organogel constructed from a DNA/lipid complex.

EXPERIMENTAL

A stoichiometric complex of DNA sodium salt and *N,N,N*-trimethyl-*N*-hexadecylammonium bromide (THAB) was prepared by mixing an aqueous solution of salmon sperm DNA (purchased from the Sigma Chemical Co., St. Louis, MO; $M = 1.2 \times 10^6$, ca. 2000 bp, $c = 10$ mg/mL) and THAB in a test tube at room temperature. The obtained complex precipitate was separated from the supernatant by centrifuging, then decanted and freeze-dried. One gram of white powder was dissolved in dimethyl sulfoxide (DMSO) at 65°C, and 0.2 g of isophorone diisocyanate (IPDI) was added dropwise with vigorous stirring. The mixture was poured into a frame mold and cured in a vacuum oven at 60°C for film formation.

FTIR spectra of the original DNA, THAB, and uncrosslinked and crosslinked complex samples are shown in Figure 1. For THAB, the absorbance bands at 2918 and 2850 cm^{-1} are assigned to characteristic peaks of —CH2— and —CH3, while DNA exhibits the absorbance bands of base pairs at 1602 cm^{-1} (adenine), 1660 cm^{-1} (thymine), 1690 cm^{-1} (guanine), and 1481 cm^{-1} (cytosine).[16] The absorbance of phosphate ester is located at 1236 cm^{-1}. From Figure 1(c), it can be seen that there exist strong absorbance bands at 2919 and 2850 cm^{-1} and characteristic bands of DNA, suggesting the formation of a DNA/lipid complex. In contrast, for the crosslinked complex, the new bands at 2843 and 1052 cm^{-1} are originated from a symmetry stretching vibration of —CH_3 on the cyclohexane ring of IPDI and the vibration of the ring itself. Furthermore, no absorbance of NCO (2270 cm^{-1}) is observed, indicating that NCO groups take part in the reaction. In addition, the band centered around 1642 cm^{-1} is evidence of the absorbance of C═O in urea.

The structures of DNA, THAB, and IPDI are exhibited in Figure 2. From the structures of the reactants and the above

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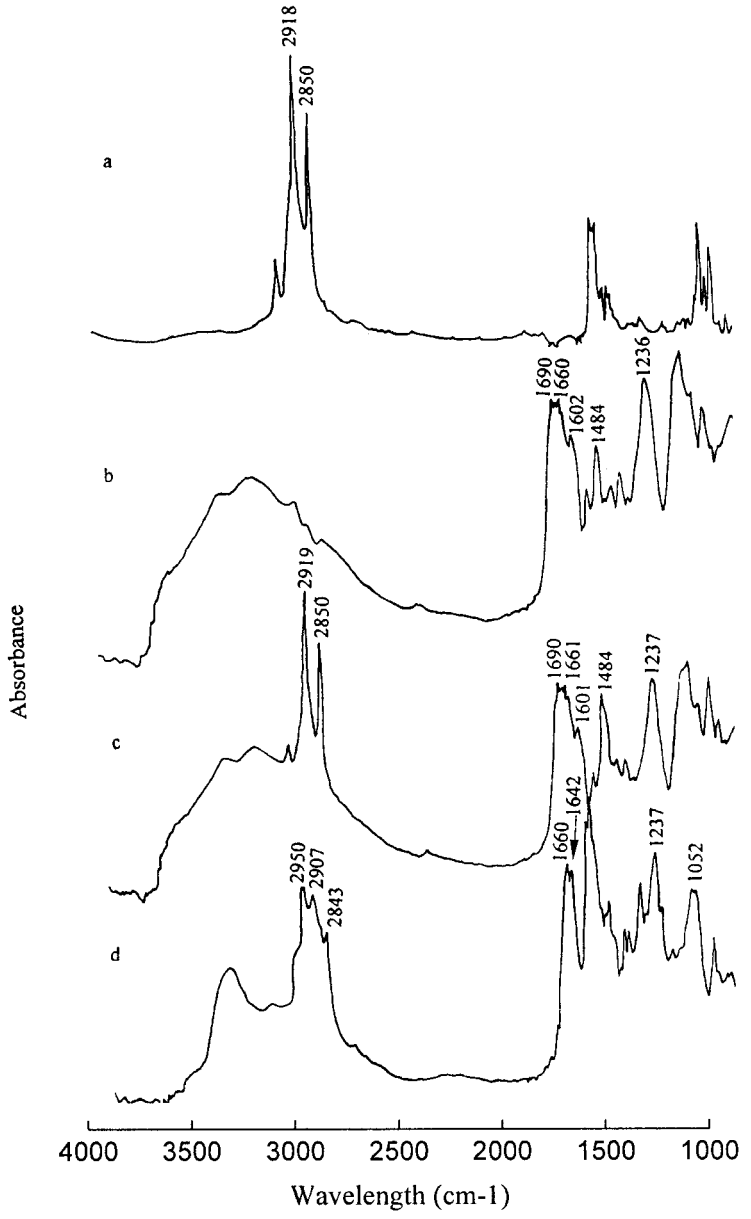
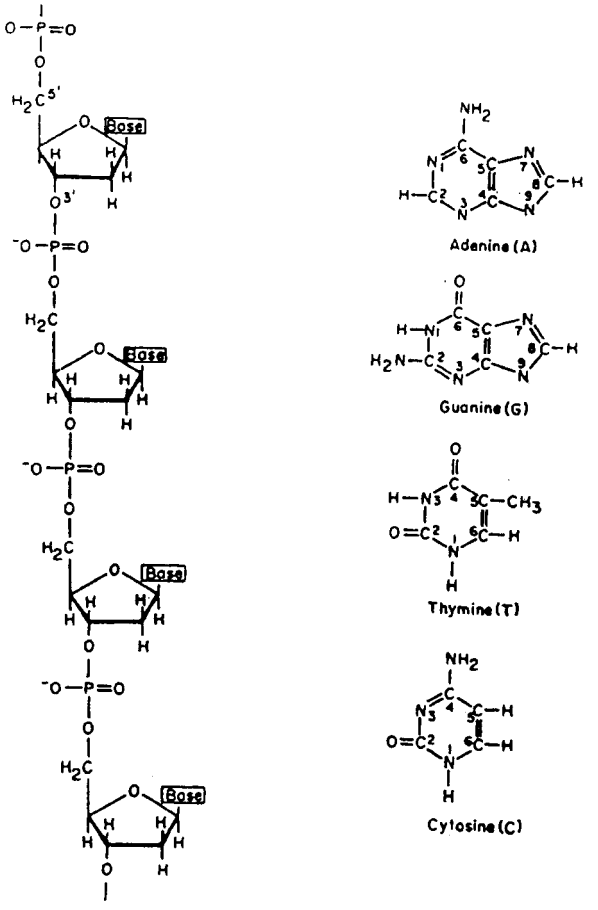


Figure 1 FTIR spectra of (a) THAB, (b) original DNA, (c) uncrosslinked complex, and (d) crosslinked complex samples.

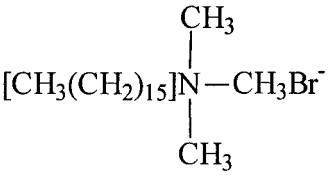
analysis, it is reasonable to consider that the NCO group reacts with ammonium groups on A, G, and C base pairs to form urea crosslinks. It is most probable that there exist intrastrand, interstrand, and interhelical crosslinks due to the possibility of the reaction between NCO and NH_2 on different sites of base pairs.

For the equilibrium swelling degree measurement at different temperatures, dried crosslinked complex samples of known weight were immersed into the sealed DMSO at a fixed temperature for 24 h. Then, the samples were removed from the liquid and blotted with filter paper to remove the solvent on the surface. The samples were weighted on a microbalance, and $W_S - W_0/W_0$ was used to evaluate the equilibrium swelling degree (ESD), where W_S and W_0 are the weight of the wet and dried samples, respectively. Figure 3 shows the dependence of ESD on the temperature. As shown in the figure, the ESD varies only slightly with increase of the temperature until 65°C, at which a discontinuous variation occurs.

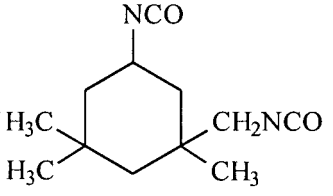
In the temperature range from 25 to 90°C, we investigated the turbidity variation in the DMSO solution of the complex by measuring the absorbance at the wavelength of 620 nm. Figure 4 displays the absorbance of a 1% DMSO solution of the DNA/lipid complex as a function of temperature. From the figure, it can be seen that at temperatures to 65°C the absorbance remains high, and in this case, the DNA/lipid complex is insoluble. As the temperature is increased, the absorbance slightly decreases; at 65°C, the absorbance decreases significantly, and at this time, since the complex is completely dissolved, the solution becomes transparent. From the turbidity measurement, it is considered that the upper critical solution temperature (UCST) of the DNA/lipid complex is 65°C. Therefore, the phase-transition temperature of the crosslinked complex is related to the UCST of the complex solution.



DNA



THAB



IPDI

Figure 2 Structure of reactants.

It is noticed that a trace amount of water could cause the gel to shrink. Hence, the crosslinked DNA/lipid complex is called an organogel. Interestingly, we observed that the organogel can "memorize" its initial shape-varying temperature. Above 65°C, the swollen soft gel is stretched to 1.8 times its initial length under a fixed load, and then when the temperature is decreased to 25°C, the gel becomes rigid. After equilibrium is established, with the load being removed, the gel can retain the stretched length. As the temperature is increased above 65°C, the gel can recover its

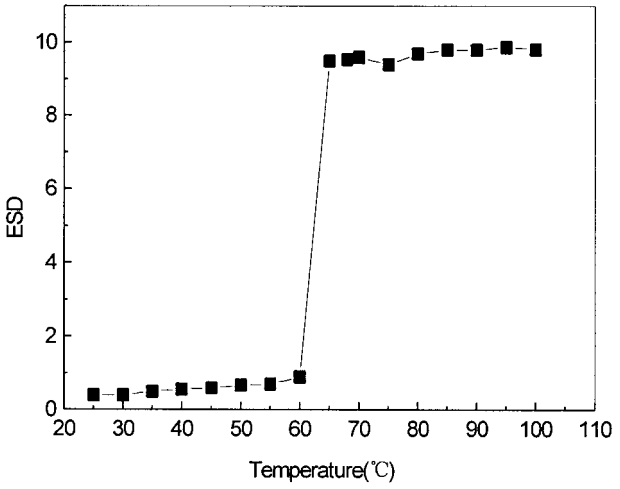


Figure 3 Equilibrium swelling degree of organogel as a function of temperature in DMSO.

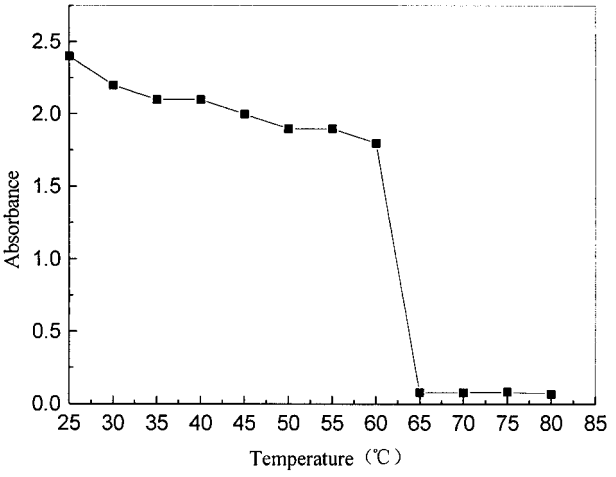


Figure 4 Absorbance of 1% DMSO solution of DNA/lipid complex versus temperature.

original length. To our surprise, whatever the shape the gel is deformed to, it always "memorizes" its initial shape once the temperature is enhanced again to 65°C.

Figure 5 shows one example of the gel's shape-memory behavior. To observe the variation process clearly, the gel was dyed. It is noted that dyeing does not affect the memory behavior. The gel sample is first heated to 65°C and then cut into three capital letters: "DNA" [Fig. 5(A)]. At 65°C, the DNA letters are deformed to three "bars" and cooled to 25°C. As shown in Figure 5(B), the gel retains the bar shape. As the temperature is increased to 65°C, the bars recover their initial shape: "DNA" letters [Fig. 5(D)], from the intermediate process [Fig. 5(C)].

CONCLUSIONS

We think that the shape-memory behavior of the organogel is closely associated with the change of the phase in the microscale. Below 65°C, since the gel expels most of the solvent, the DNA/lipid strands become more rigid and stacked, and, moreover, the high polar urethane crosslinking bonds between base pairs act as a fixed phase, which makes the gel retain a certain shape. Above 65°C, along with the permeation of the solvent, the close-packed DNA/lipid conformation is destroyed and the network is expanded and readily deformed. Importantly, the built-in elastic urethane crosslinking bonds render the organogel reversible.

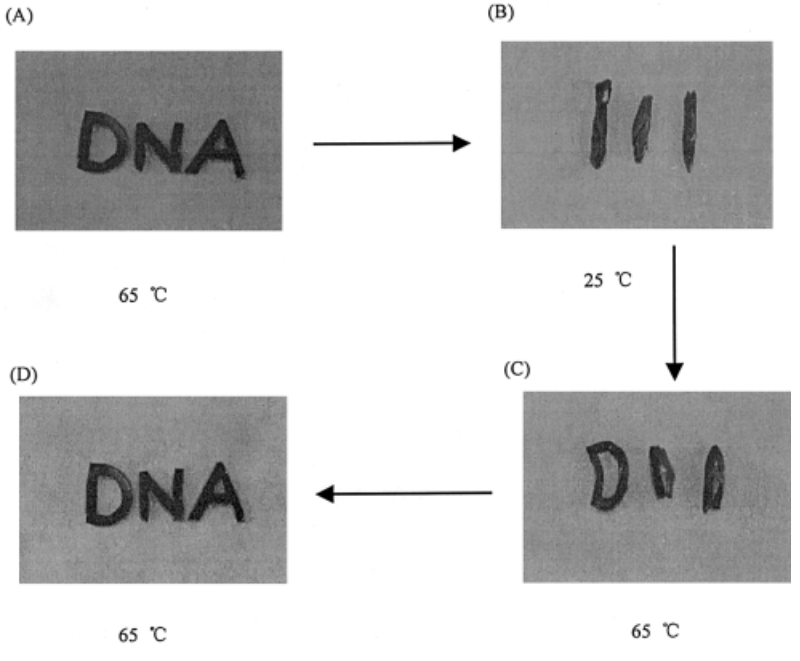


Figure 5 One example of the organogel's shape-memory behavior.

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