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ORIGINAL CONTRIBUTION

Thermotropic liquid-crystal/polymer microcapsules prepared by in situ suspension polymerization

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Abstract In this study, thermotropic liquid-crystal/polymer microcapsules were produced via in situ suspension polymerization. The phase separation between cholesteryl liquid crystal (CLC) and poly(methyl methacrylate) (PMMA) in the droplets was induced by polymerization, resulting consequently in uniform liquid-crystal-containing polymer microcapsules. The phase behavior of the microcapsules was dependent on the loading amount of the liquid crystals and the degree of cross-linking of the polymer phase. Above 30% loading amount of CLC, the liquid crystals started to appear clearly. It was found that the spherical morphology of the microcapsules was achieved within a slight degree of cross-linking of the PMMA phase. At a high degree of cross-linking, nonspherical particles with a rough surface and deeper dents were obtained, which was due to the elastic-retractive force of the cross-linked network. The liquid-crystal/polymer microcapsules produced in this study could find great applicability in pharmaceutics and electronics as a smart drug carrier.

Keywords Thermotropic · Liquid crystals · Microcapsules · Phase separation · Elastic-retractive force

Introduction

Microcapsules have been applied to a wide range of products, such as foods, pharmaceuticals, agrochemicals and cosmetics owing mainly to their characteristics of controlled release and ability to protect environmental stimuli [1, 2, 3, 4, 5]. Usually, they were developed by employing various methods, including coacervation phase separation, interfacial polymerization, solvent evaporation, spray coating, multiorifice centrifugal process and air suspension [6, 7, 8, 9]. In these methods, the encapsulation process is simple and the phase separation between the core and the capsule shell takes place simultaneously during the process.

Nowadays, as the use of liquid crystals becomes important, studies have been carried out in many liquid-crystal systems for electrooptics and thermographics [10, 11]. Especially, thermotropic liquid crystals (cholesterol-based derivatives) have been employed usefully as a substrate in intelligent drug delivery system [12, 13, 14, 15]. In these studies, it was shown that the phase transition of liquid crystals was characterized by the composition of the liquid crystals and outer stimuli (temperature and pH). However, in some other applications, the possible dependence of the liquid crystals on the outer stimuli can be a fatal defect in ultimate applications. Therefore, there have been investigations of new liquid-crystal materials using polymers and liquid crystals [16, 17, 18]. Here in this study, we introduce a useful liquid-crystal system employing the technique of microencapsulation. It is a well-known fact that the encapsulation of liquid crystals in the polymer substrate is very difficult, because the intrinsic characteristics of liquid crystals disappear upon adding solvent or dilution. Until now, actually, microcapsules loading uniform liquid crystals in the inner core have not been reported in the literature.

In the present contribution, we synthesized thermotropic cholesteryl liquid crystal (CLC) microcapsules by in situ suspension polymerization. It was attempted to systematically understand the morphology and phase behavior of the liquid-crystal microcapsules produced.

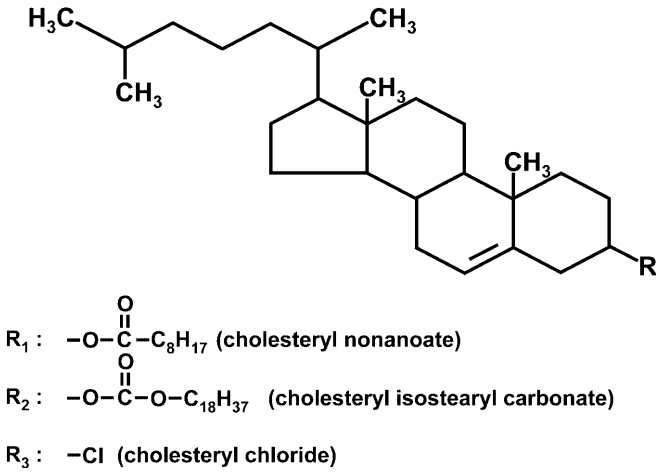
Experimental

Materials

The CLC used was a mixture of cholesteryl nonanoate (46 wt%), cholesteryl isostearyl carbonate (30 wt%), cholesteryl chloride (20 wt%) and squalane (4 wt%) (Scheme 1). Methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA), sodium nitrite and methylene chloride (MC) were all reagent grade and were purchased from Aldrich Chemical Co. Poly(vinyl alcohol) (PVA, $M_w = 8.8\times10^4$–9.2×10^4 gmol^{-1}, 87–89% degree of saponification) was kindly supplied by Kuraray Co. 2,2-Azobis(2,4-dimethylvaleronitrile) (ADVN, Wako Pure Chemicals) was recrystallized from methanol before use.

Preparation of CLC/poly(MMA) microcapsules

The thermotropic CLC/poly(MMA) (PMMA) microcapsules were produced by in situ suspension polymerization. CLC, MMA and EGDMA were mixed freely with MC in a volume ratio of 4:1. The concentration of initiator, ADVN, was fixed to 1 wt% against the total monomer weight. The CLC/monomer/initiator/MC solution prepared was poured into 1.5 wt% PVA aqueous solution and emulsified with a homogenizer at 5,000 rpm for 5 min. The final suspension yield in the total formulation was adjusted to 10 wt%. Then, polymerization was carried out in a double-walled glass reactor equipped with a stirrer, a reflux condenser, thermocouples and a nitrogen gas inlet system. The agitation speed was fixed at 250 rpm throughout the process. The polymerization in the aqueous phase was inhibited by adding sodium nitrite (0.01 wt%). After deaerating with nitrogen gas, the polymerization was carried out at 60 °C for 4 h. The particles produced were washed repeatedly by decantation in water and ethanol and dried under a vacuum at ambient temperature. The composition and designation of each sample are listed in Table 1.



Scheme 1 Structures of cholesteryl nonanoate, cholesteryl isostearyl carbonate and cholesteryl chloride

Table 1 The designation of cholesteryl liquid crystal (*CLC*)/poly(methyl methacrylate) (*PMMA*) microcapsules. 60 °C, 4 h, 250 rpm, 1 wt% 2, 2-azobis(2,4-dimethylvaleronitrile) based on total monomer weight

System[a]	Composition (wt%)		
	CLC	MMA	Ethylene glycol dimethacrylate
CLC100X0[b]	100	–	–
CLC10X0.5	10	89.5	0.5
CLC30X0.5	30	69.5	0.5
CLC50X0.5	50	49.5	0.5
CLC30X0	30	70	–
CLC30X0.1	30	69.9	0.1
CLC30X1	30	69	1
CLC0X0[c]	–	100	–

[a]CLCαXβ: α is the concentration of CLC in the microcapsules, β is the concentration of ethylene glycol dimethacrylate in the polymer phase
[b]Pure CLC
[c]Pure PMMA

Characterization

The apparent liquid-crystal images of the microcapsules produced were observed with an optical microscope (OM, Nikon) and a polarized optical microscope (POM, Nikon). Differential scanning calorimetry (DSC, TA Instruments, DSC 910) was used to measure the phase-transition temperature, T_t. DSC traces were recorded from 20 to 100 °C with a heating rate of 5 °C/min under nitrogen flow. The crystallinity of the CLC/PMMA microcapsules was investigated by X-ray diffraction (XRD, Riguka Denki, model RAD-C) in the 2θ range from 5 to 40°. The surface image of the microcapsules was observed with a scanning electron microscope (SEM, Hitachi S-4300).

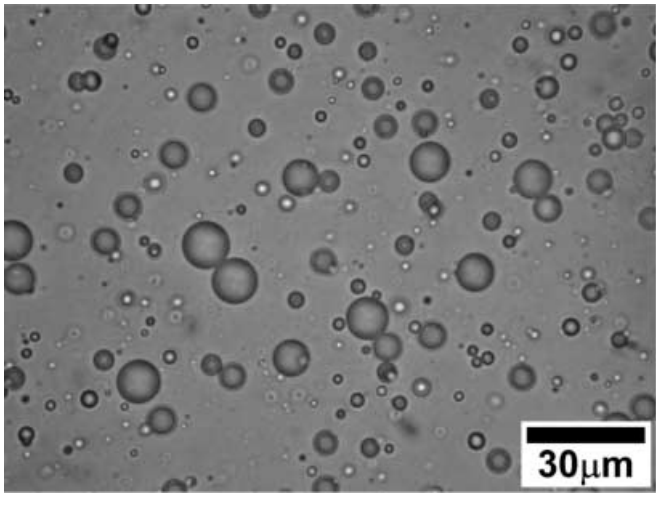


Fig. 1 Optical microscope images of CLC30X0.5 droplets in 1.5% poly(vinyl alcohol) aqueous solution at 25 °C. CLCαXβ: α is the concentration of cholesteryl liquid crystal (*CLC*) in the microcapsules, β is the concentration of ethylene glycol dimethacrylate in the polymer phase

Table 2 The thermal and morphological characteristics of CLC/PMMA microcapsules. The 2θ values were obtained by X-ray diffraction measurements. The transition temperature, T_t, was determined by differential scanning calorimetry analysis

System	2θ (°)			T_t (°C)	Remarks
	$2\theta_1$	$2\theta_2$	$2\theta_3$		
CLC	16.75	–	–	46.8, 53.5	
CLC10X0.5	14.95	30.60	41.85	–	Sphere, smooth surface
CLC30X0.5	16.80	30.85	41.90	49.1	Sphere, rough surface, small dimple
CLC50X0.5	16.85	–	–	47.9	Sphere, rough surface, heavy dent
CLC30X0	16.70	30.75	41.75	48.7	Sphere, smooth surface
CLC30X0.1	16.90	30.55	41.65	49.0	Sphere, smooth surface
CLC30X1	16.80	30.70	41.90	48.8	Ellipse, heavy dent
PMMA	14.35	30.85	42.10	–	Sphere, smooth surface

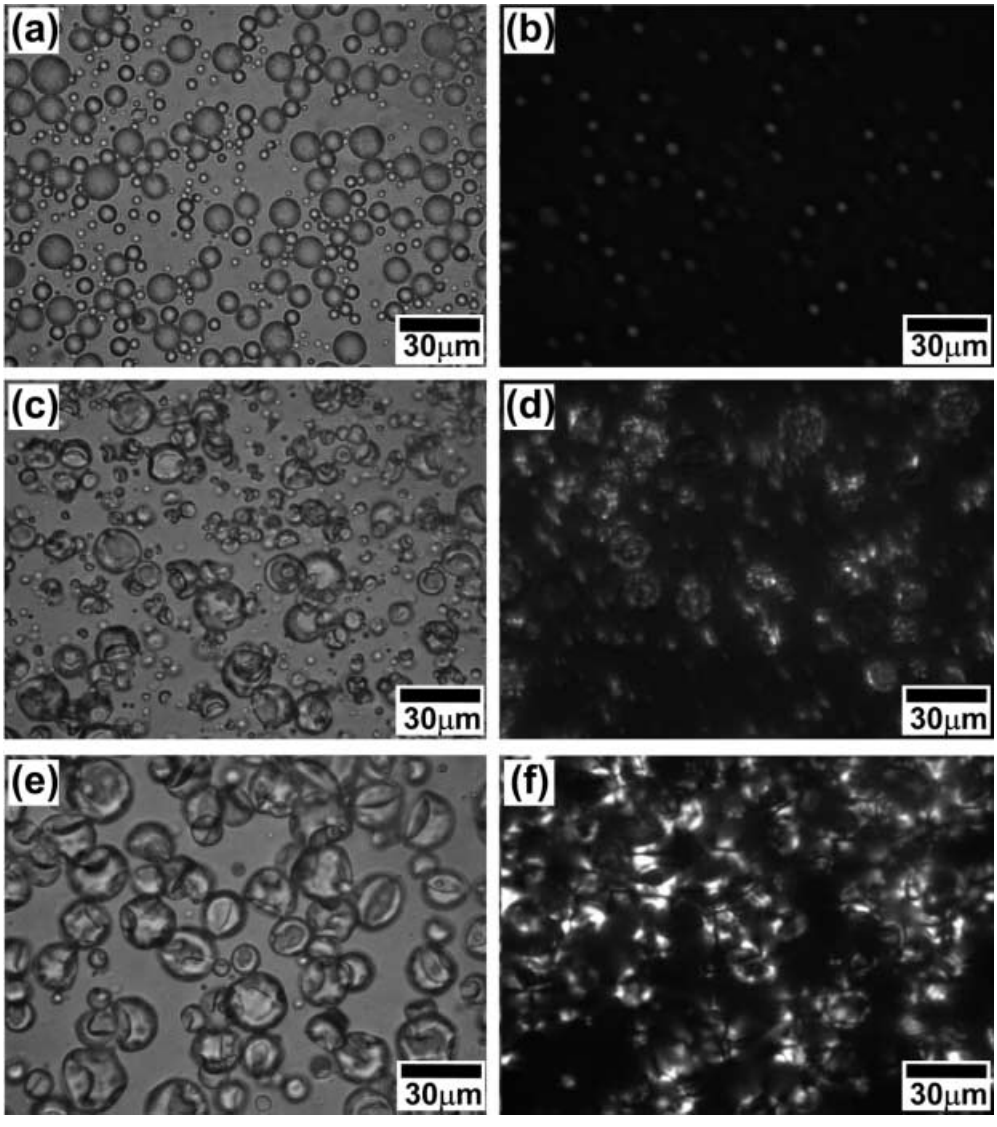


Fig. 2 Optical microscope images of **a** CLC10X0.5, **c** CLC30X0.5 and **e** CLC50X0.5 and polarized microscope images of **b** CLC10X0.5, **d** CLC30X0.5 and **f** CLC50X0.5. The images were taken at 25 °C

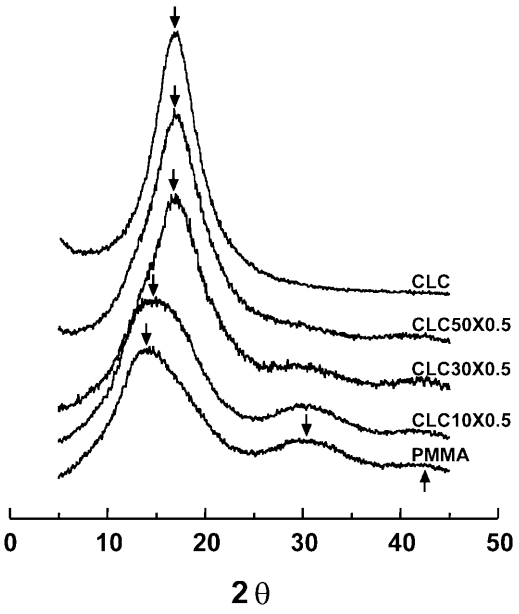


Fig. 3 X-ray diffractograms of CLC, CLC50X0.5, CLC30X0.5, CLC10X0.5 and poly(methyl methacrylate) (*PMMA*). The measurement was carried out at 25 °C

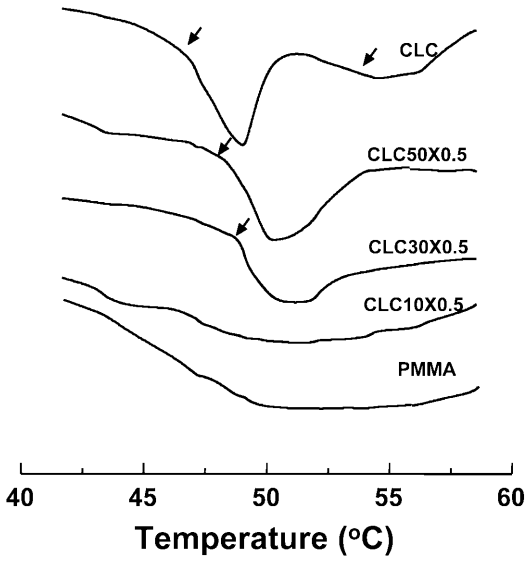


Fig. 4 Differential scanning calorimetry thermograms of CLC, CLC50X0.5, CLC30X0.5, CLC10X0.5 and PMMA

Results and discussion

Characteristics of CLC/PMMA microcapsules

In this study, thermotropic CLC/PMMA microcapsules were obtained by in situ suspension polymerization. In the initial dispersion, the droplets composed of CLC and monomers were dispersed in an aqueous solution. An OM photograph of the PVA-stabilized CLC/monomers droplets in water at 25 °C is shown in Fig. 1. As shown, the droplet phase was homogeneous, meaning all the components mixed freely in the dispersion state. However, as the monomer components in the droplets were polymerized at high temperature, phase separation took place as a result of the decrease in the miscibility between CLC and PMMA. The CLC/PMMA microcapsules obtained had a capsule structure where CLC was encapsulated in the PMMA particles. The morphology of the microcapsules was considerably dependent on the degree of cross-linking of the PMMA phase. From the OM and POM observations, it was clarified that CLC was located in the form of inner domains in each PMMA particle. The size of the CLC/PMMA microcapsules was in the range 3–15 μm. The overall characteristics of the CLC/PMMA microcapsules are summarized in Table 2.

Effect of loading amount of CLC

The CLC/PMMA microcapsules with various loading amount of CLC were observed with an OM and a POM, as shown in Fig. 2. As mentioned, it is obvious in Fig. 2 that the microcapsules have the morphology of CLC in PMMA particles. Below 10 wt% CLC concentration, the intrinsic property of the liquid crystals was not observed. However, as the amount of CLC in the microcapsules increased, one could see the CLC phase more distinctly. One of main reasons for such results could be found in the phase separation between CLC and PMMA during polymerization. The phase behavior of CLC started to appear significantly above 30 wt% loading amount of CLC in PMMA. However, microcapsules were not produced above 70 wt% CLC concentration, because the high volume ratio of CLC to PMMA led to the leakage of CLC out of the particles. From those results, it is reasonable to estimate that the proper loading amount of CLC was 30–50 wt%.

The XRD pattern to confirm the crystallinity of CLC/PMMA microcapsules with different loading amounts of CLC in PMMA is shown in Fig. 3. The characteristic 2θ of CLC was 16.75° and of PMMA was 14.35, 30.85 and 42.10°, respectively. When the loading amount of CLC was small, 2θ of the microcapsules was almost similar to that of PMMA; however, as the amount of CLC increased, $2\theta_1$ of the microcapsules shifted toward 16.75°, which is in accordance with that of CLC. From the XRD pattern, it is explained the crystallinity of the CLC/PMMA microcapsules was attributed to the respective properties of CLC and PMMA, which stemmed from the clear phase separation in the microcapsules.

It is well known that the transition temperature, T_t, of a mixed system depends on the characteristics of the components and their phase morphology [19]. The results of DSC measurements are exhibited in Fig. 4.

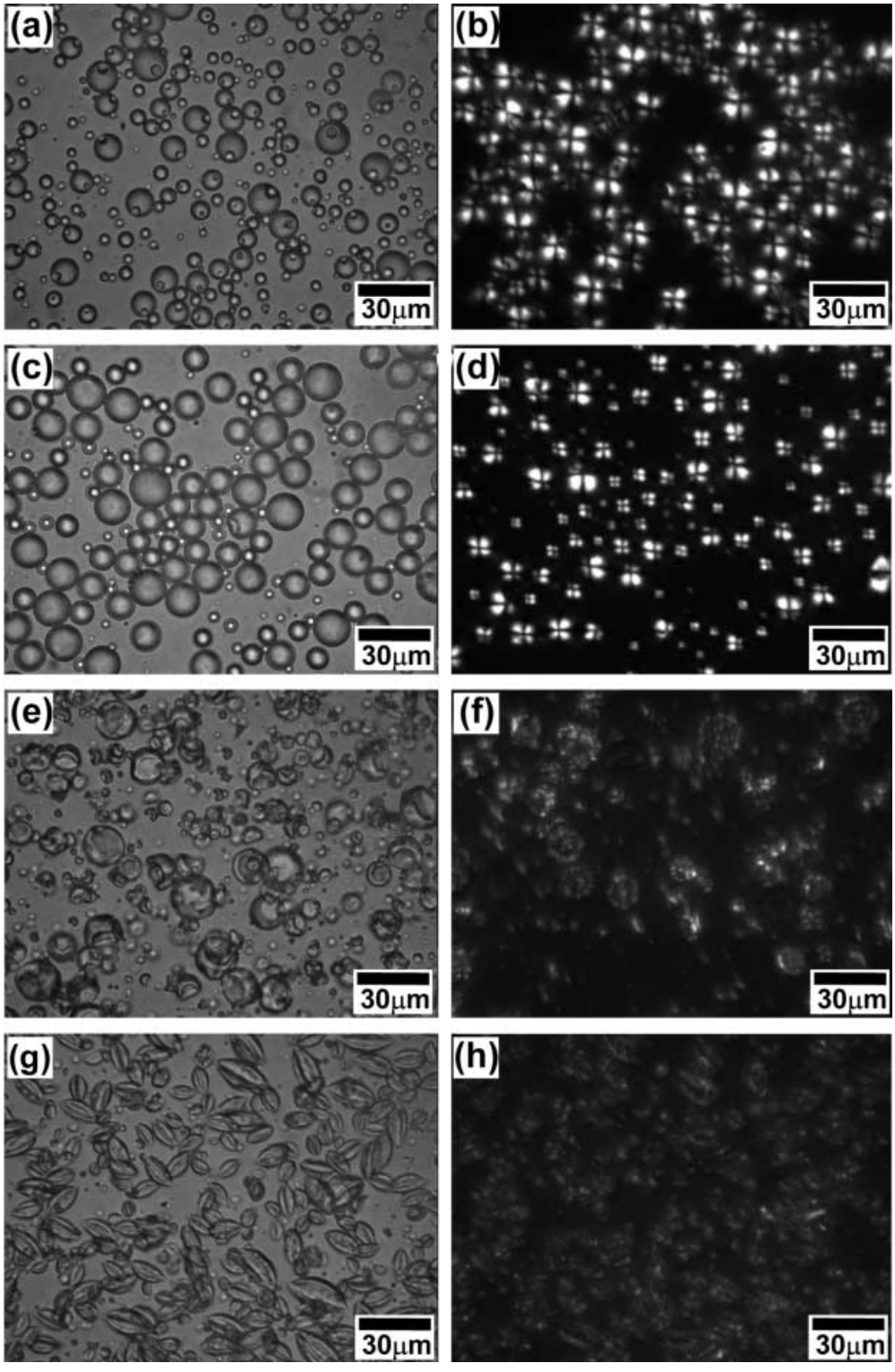


Fig. 5 Optical microscope images of **a** CLC30X0, **c** CLC30X0.1, **e** CLC30X0.5 and **g** CLC30X1 and polarized microscope images of **b** CLC30X0, **d** CLC30X0.1, **f** CLC30X0.5 and **h** CLC30X1. The images were taken at 25 °C

The endothermic peaks of CLC were detected at 46.8 and 53.5 °C, respectively. Considering that CLC is composed of ternary CLCs, the two peaks correspond to the solid-cholesteryl transition and the cholesteryl-isotropic transition [20, 21]. In the state of microencapsulation, the thermotropic behavior of CLC was quite different. In the DSC thermograms, 10 wt% CLC-containing microcapsules did not display any T_t

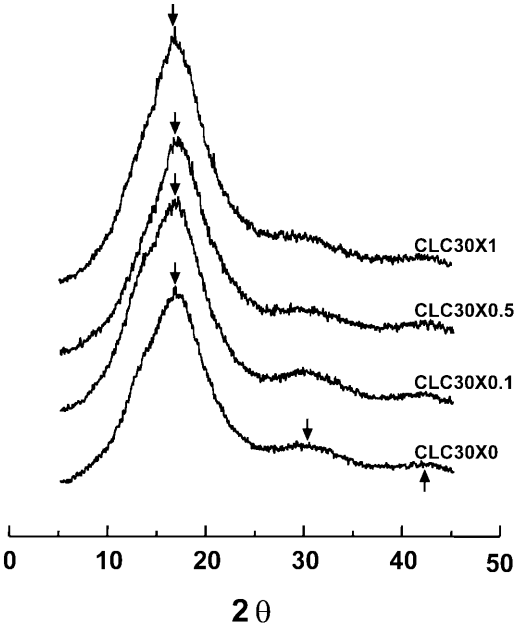


Fig. 6 X-ray diffractograms of CLC30X0, CLC30X0.1, CLC30X0.5 and CLC30X1. The measurement was carried out at 25 °C

over the temperature range between 40 and 60 °C, just like the case of PMMA. Relative to that phenomenon, it is assumed that the phase mixing between CLC and PMMA happened because of the effect of the phase volume. However, above 10 wt% concentration of CLC in the microcapsules, T_t started to appear in the DSC thermograms. This peak is ascribed as a solid-cholesteryl transition [14]. Moreover, T_t shifted toward a low temperature with the increase in the CLC concentration. Judged together with the XRD data shown in Fig. 4, it can be said that for an appropriate CLC/PMMA composition, the phase separation between CLC and PMMA happened effectively.

Effect of degree of cross-linking

To obtain structurally stable microcapsules, the cross-linking of the PMMA phase can be suggested. Therefore, the effect of cross-linking on the formation of microcapsules was observed. As shown in Fig. 5, the increase in the degree of cross-linking resulted in non-spherical microcapsules, probably ellipsoidal particles. In the POM image, the characteristics of the liquid crystals were vague, as the degree of cross-linking increased. It appears that the deformed surface of the microcapsules screened the phase behavior of CLC. However, in the XRD measurements shown in Fig. 6, it can be observed that the peaks were sharpened according to the increase in the degree of cross-linking,

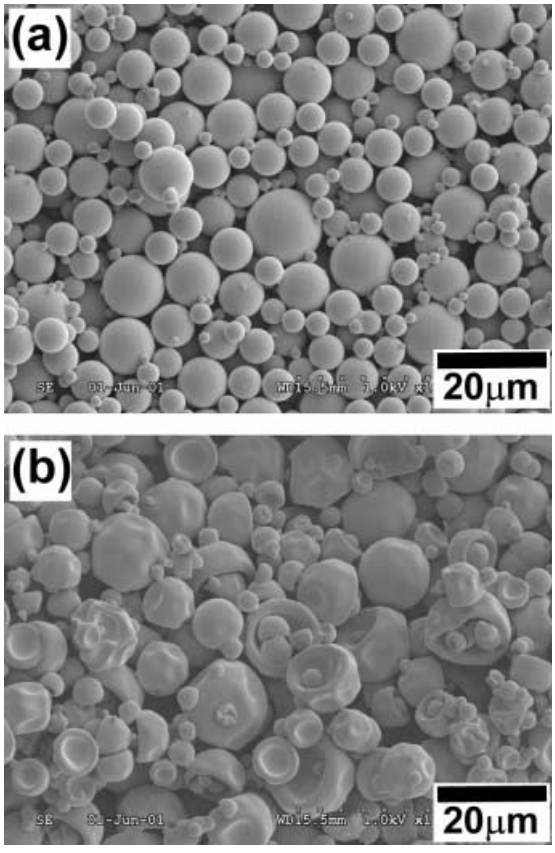


Fig. 7 Scanning electron microscope photographs of **a** CLC30X0 and **b** CLC30X0.5

meaning that the higher cross-linking density of the polymer phase in the microcapsules induced a more effective buildup of crystallinity of CLC. The phase separation between CLC and PMMA takes place by the reduction of compatibility, which is made by controlling the degree of polymerization of PMMA. In the case of cross-linking, the degree of polymerization is maximized, resulting in more favorable phase separation of CLC in the PMMA phase.

An SEM image of the CLC/PMMA microcapsules is shown in Fig. 7. The non-cross-linked or slightly cross-linked microcapsules were very spherical and had a smooth surface. On the other hand, the microcapsules cross-linked with a relatively large amount of crosslinker had a rough surface and many dents. It is believed that the irregular morphology at a high cross-linking density is attributed to the elastic-retractive force in the cross-linking network [22, 23]. The polymer network has a tendency toward shrinking at a high temperature. In this study, the cross-linking of PMMA was carried out at a high polymerization temperature, 60 °C. Therefore, the elastic-retractive force created in the polymerization process is capable of deforming the capsule morphology. Furthermore, the deformation of the capsule morphology takes

place readily by the presence of soft CLC domains in the PMMA particles. Considered on the basis of our results, it is suggested that a slightly cross-linked network system is useful for the achievement of spherical morphology and to some extent strong mechanical properties.

Conclusions

CLC/PMMA microcapsules with various cholesterol loading amounts and different cross-linking concentration were produced by in situ suspension polymerization. The phase behaviors of CLC in the PMMA microcapsules measured by XRD and DSC started to appear 30 wt% CLC concentration. In the morphological observation, it was confirmed that the microcapsules were composed of a CLC core and a PMMA shell, showing the mononuclear capsule morphology. As another factor influencing on the behavior of liquid-crystal in the microcapsules, we propose the cross-linking of the polymer phase. From XRD and DSC analysis, it was deduced that although the apparent image of CLC in the microcapsules was somewhat vague because of the deformed morphology, the phase separation between CLC and PMMA was induced more obviously by the increase in the degree of cross-linking. These CLC/PMMA microcapsules could be applied to optical devices in electronics and thermoresponsive drug carriers in pharmaceutics.

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