

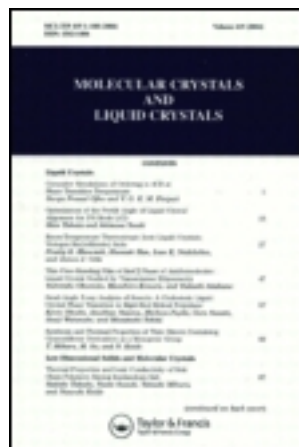
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NOVEL PDLC FILMS BASED ON A PHOTOACTIVE POLYMERIC BINDER

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We report the synthesis and characterization of a novel polymeric material which has been used as binder in the fabrication of PDLC films. A monomer bearing a carbazolyl moiety has been copolymerized, using azobisisobutyronitrile (AIBN) as initiator, with a monomer containing a mesogenic core. PDLC films have been prepared using copolymers with different composition in the two monomers. A detailed morphological analysis has been carried out to evaluate a correlation between the copolymer composition and the PDLC film morphologies.

Keywords: PDLC film; optical storage; radical copolymerization

INTRODUCTION

PDLC (Polymer Dispersed Liquid Crystal) films are inhomogeneous composite materials in which low molar mass liquid crystals are randomly dispersed in a polymeric matrix [1].

Interest on these systems has arisen because of their employment in the fabrication of optical devices such as switchable windows, light valves, displays.

In recent years the possibility of using PDLC films as optical storage media has faced out as well, making these materials even more attracting [2].

The combination of photoconducting and electro-optic properties, achievable through the use of PDLCs, seems to be promising for the development of new optical memories [3].

In these materials an inhomogeneous illumination of the sample under the application of an electric field generates a spatial redistribution of the charges and consequently a refractive index modulation due to the reorientation of the liquid crystal domains throughout the sample. This effect can then be used to store an optical information in the PDLC film.

In this article we describe the synthesis and characterization of a novel polymeric material which has been used in PDLC fabrication with the aim of exploiting further these devices as optical storage media.

We used a methacrylate bearing a carbazoyl unit (**1**) and a methacrylate with a mesogenic core (**2**) as comonomers (Scheme 1). Monomer **1** is responsible for the peculiar electric properties of the matrix since carbazoyl unit can be photo-oxidized and, under the application of an electric field, the electrons are allowed to move across the bulk of the film.

A key-point in designing a new polymeric material for PDLC preparation is the stabilization of the liquid crystal domains. In fact the electro-optical properties and hence the possible marketing of such devices are deeply influenced by the integrity of the films over a long period of time.

This stabilization can be ensured using a comonomer with the same mesogenic unit of the liquid crystal mixture used for the preparation of PDLC films. In this way it is possible to get areas in the polymeric matrix towards which the liquid crystal molecules should have a greater chemical affinity and then the tendency to segregate themselves there. This means that it should be possible to control the sizes of liquid crystal domains simply by varying the amount of mesogenic monomer in the copolymer.

Some attempts have already been tried to prepare PDLC using a birefringent matrix [3,4]. In fact using a birefringent matrix it is possible a better index matching between polymer and liquid crystal domain with the consequence of reducing the haze phenomenon.

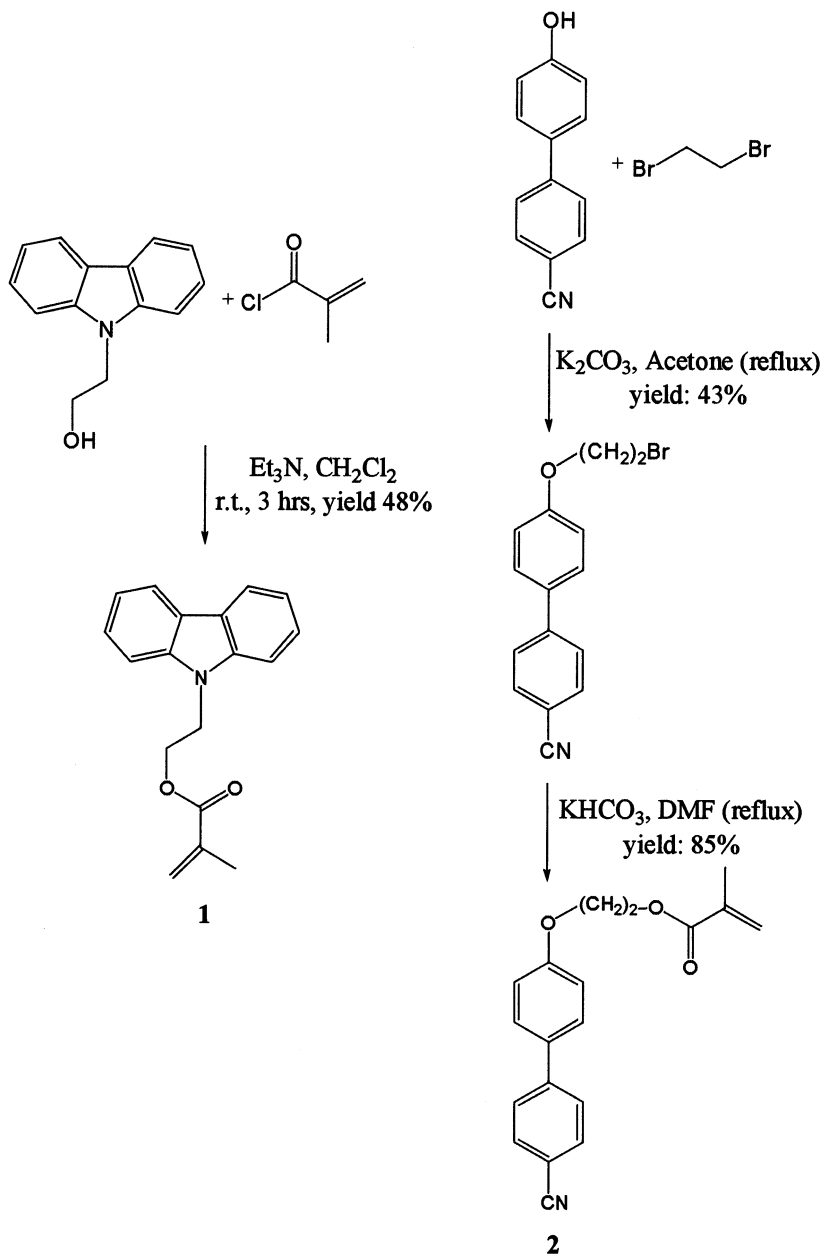
Accordingly we used as comonomer a methacrylate with a cyanobiphenyl group.

Several PDLC samples were prepared using as a binder copolymers with different composition in the two comonomers. A detailed investigation has been carried out on them using scanning electron microscopy (SEM) connected with an image analysis system to establish a correlation between the copolymer composition and the PDLC film morphologies.

EXPERIMENTAL PART

Materials

Methacryloyl chloride (Fluka), triethylamine and THF (Fluka) were distilled. Acetone was refluxed overnight on K_2CO_3 and then distilled. 1,2-dibromoethane was distilled. Benzene (Fluka), N-hydroxyethylcarbazole



SCHEME 1

(Aldrich), 4-hydroxy-4'-cyanobiphenyl (Aldrich), hydroquinone (Aldrich), methacrylic acid (Fluka) and N,N-dimethylformamide (Merck) were used as received. AIBN was recrystallized by methanol.

Synthesis of N-(2-hydroxyethyl)carbazolyl Methacrylate (**1**)⁵

The amount of 3.96 g (18.6 mmol) of N-hydroxyethylcarbazole was dissolved in 100 ml of benzene in a three-neck round bottom flask, equipped with dropping funnel and under inert atmosphere. 3.10 ml (22.2 mmol) of triethylamine were added. The solution was cooled by mean of an ice-bath and, under vigorous stirring conditions, 2.10 ml (22 mmol) of methacryloyl chloride were added dropwise over a time of 20 min. After one hour the ice-bath was removed and the reaction let for two hours at room temperature.

Then ammonium chloride was filtered off and the organic phase was washed with NaOH 5% and water. The organic layer was dried over Na₂SO₄ and the solvent was evaporated. The product was recrystallized by methanol to yield 2.5 g (8.9 mmol) of **1** (yield: 48%).

IR (KBr) ν/cm^{-1} : 1719.2 (C=O).

¹H-NMR (CDCl₃): δ 7.90 (2H, aromatic), 7.25–7.04 (6H, aromatic), 5.71 (1H, vinylic), 5.26 (1H, vinylic), 4.41–4.32 (4H, -CH₂CH₂-), 1.59 (3H, methyl).

¹³C (CD₂Cl₂): δ 167.37, 140.83, 136.26, 126.23, 126.11, 123.27, 120.60, 119.53, 109.13, 62.90, 18.32.

Synthesis of 1-bromo-2-(4'-cyanobiphenyl-4-yloxy)ethane⁶

The amount of 2.72 g (13 mmol) of 4-hydroxy-4'-cyanobiphenyl and 21.8 g (116 mmol) of 1,2-dibromoethane were added to a well-stirred suspension of K₂CO₃ (13.47 g, 97.5 mmol) in 150 ml of dry acetone in a three-neck round bottom flask, under inert atmosphere. The solution was refluxed overnight. The solution was filtered hot and the residue washed with acetone; solvent and unreacted 1,2-dibromoethane were removed under reduced pressure. The residue was chromatographed on silica gel (eluant: petroleum ether/ethylacetate = 8/2) and the second collected fraction was recrystallized by ethanol to give 1.697 g (5.6 mmol) of 1-bromo-2-(4'-cyanobiphenyl-4-yloxy)ethane (yield: 43.2%).

¹H-NMR (CD₂Cl₂): δ 7.73–7.56 (6H, aromatic), 7.04–7.0 (2H, aromatic), 4.35 (2H, -CH₂O), 3.69 (2H, -CH₂Br).

¹³C (CD₂Cl₂): δ 159.09, 145.13, 132.89, 132.41, 128.76, 127.37, 119.26, 115.53, 110.57, 68.37, 29.82.

Synthesis of 2-(4-cyanobiphenyl-4'-yloxy)ethyl Methacrylate (**2**)

The amount of 0.183 g (2.13 mmol) of methacrylic acid and 0.183 g (2.04 mmol) of KHCO_3 were stirred to form the salt, in a double-neck round bottom flask, under inert atmosphere. 0.437 g (1.44 mmol) of compound **3** were diluted in 4 ml of *N,N*-dimethylformamide and added to the salt. Other 10 ml of DMF and a small amount of hydroquinone were added and the solution was refluxed. The reaction was monitored by thin layer chromatography and after two hours the starting material had completely reacted. On cooling the mixture was poured into water (100 ml) and well stirred to coagulate the precipitate, which was dissolved in dichloromethane.

The organic solution was washed with NaOH 5% and then with water. The organic layer was dried on Na_2SO_4 and the solvent removed under reduced pressure. The residue was purified by column chromatography (eluant: petroleum ether/ethylacetate = 8/2) to give 0.375 g (1.22 mmol) of compound **2** (yield: 84.8%).

IR (KBr) ν/cm^{-1} : 1720.4 (C=O), 1599.9 (C=C).

$^1\text{H-NMR}$ (CDCl_3): δ 7.69–7.50 (6H, aromatic), 7.02–6.98 (2H, aromatic), 6.13 (1H, vinylic), 5.58 (1H, vinylic), 4.51 (2H), 4.25 (2H), 1.93 (3H, methyl).

^{13}C (CD_2Cl_2): δ 167.40, 159.59, 145.25, 136.56, 132.91, 132.19, 128.72, 127.38, 125.92, 119.30, 115.52, 110.56, 66.54, 63.30, 18.38.

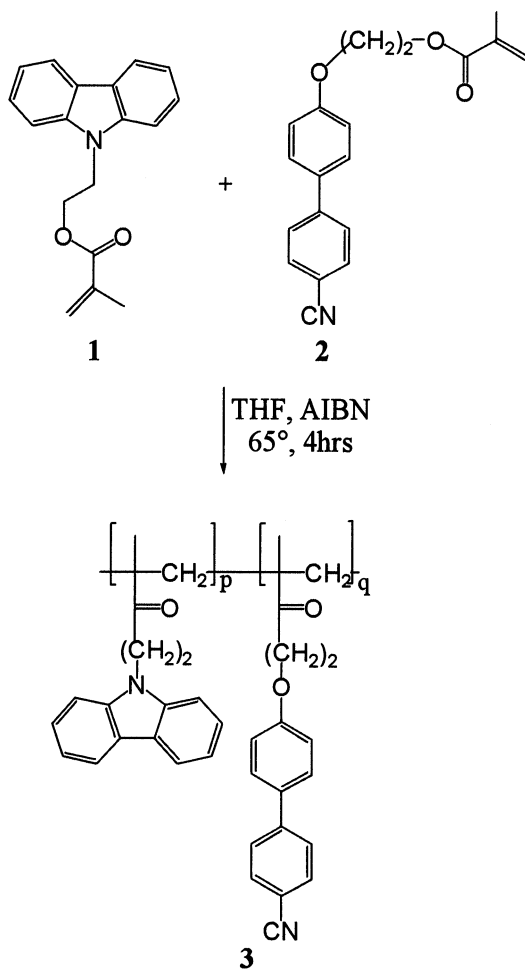
Synthesis of Copolymers Containing Carbazolyl and Cyanobiphenyl Moieties (**3**)

All copolymeric samples were prepared following the same procedure (Scheme 2).

Weighted amounts of monomer **1** and monomer **2** were dissolved in distilled THF and put in a shlenkerohr. The total concentration of the monomer was held constant at 0.4 M in each reaction. AIBN (0.25% mol with the respect to the monomers) was added. The solution was degassed using the "freeze and thaw" technique (four times) and then let under argon atmosphere. The schlenkrohr was placed in an oil bath at 65°. The reaction was stopped after four hours freezing the solution in liquid nitrogen. The solution was diluted with THF and precipitated in a large amount of methanol. Precipitation was repeated twice. The collected polymer was dried in vacuum overnight (for the conversions see Table 1).

Preparation of the PDLC Films

The PDLC samples were prepared by means of the TIPS technique [8]. A cell, which is composed by two conductive glasses (3 cm \times 1.5 cm \times 0.1 cm)



SCHEME 2

TABLE 1 Characterization of Copolymeric Samples

Sample	Conversion (%)	M_w	M_n	Dispersion	T_g
C1	70.6	63.600	27.000	2.36	139.16
C2	68.3	79.300	37.400	2.12	137.99
C2.5	63.2	70.000	35.700	1.95	135.93
C3	64	79.800	42.200	1.88	135.55

TABLE 2 Mixtures Used in PDLC Preparation

Sample code	Polymer (%)	Liquid crystal (%)	TNF (%)
M1	49 (H/1) ¹	50	1
M2	49 (C1)	50	1
M3	49 (C2)	50	1
M4	49 (C2.5)	50	1
M5	49 (C3)	50	1

¹Homopolymer obtained by radical polymerization of monomer **1**.

and kept to a defined thickness (23 μm) by Mylar spacers, was filled by capillarity at 170°, using the mixtures listed in Table 2.

The mixtures, composed by the eutectic liquid crystal mixture E7 (Merck Ltd.), copolymer **3** and 2,4,7-trinitrofluorenone (TNF) in the ratio 50:47:1, were stirred at 170° before use. After filling, the samples were put in a oven at 170° for 10 min and then were allowed to reach room temperature slowly. On cooling the mixture enters a region of the phase diagram where the homegenous solution is not stable and phase separation takes place. The obtained PDLC are opaque and strongly scatter the light.

RESULTS AND DISCUSSIONS

Synthesis and Characterization of the Copolymer

Four samples of copolymer **3**, with different compositions in the comonomers, were synthesized using radical polymerization.

The amount of monomer **2** was sistematically varied in the feed with the aim of clarifying what is the role it plays in determining the film morphology. Its amount in the feed ranged from 5% to 20% by weight. Copolymeric samples were identified, with the respect to the amount of monomer **2** in the feed, as C1 (5% by weight of **2** in the feed), C2 (10%), C2.5 (15%), C3(20%).

Conversions, weight-average molecular weight (M_w), number-average molecular weight (M_n) and glass transition temperature (T_g) for all the copolymeric samples are listed in Table 1.

As far as it can be seen, rising the concentration of monomer **2** in the feed causes an increase in polymer masses, which can be explained supposing an higher reactivity of that monomer compared to the one of monomer **1**.

In fact, usually increasing the amount of the more reactive monomer in the feed the propagation step is faster and consequently it is possible to get polymers with higher masses. Considering the chemical structures it can be

noticed that the polymerizable units are the same for both monomers. The different reactivity could then be explained claiming the steric demand of the two monomers. The steric hindrance of the cyanobiphenyl group, probably because of its rod-like shape, should be lower than the carbazoyl group's one. Then, addition of monomer **2** to the propagating species has a lower activation energy and it takes place faster. Compositional analysis of copolymeric samples, performed using NMR and UV spectroscopy, has confirmed this finding.

The molar percentage of monomer **2** in the copolymers has been determined using NMR spectroscopy by the ratio between the signal at 7.0 ppm, due to two protons of the carbazoyl moiety, and the signal at 6.7 ppm belonging to two protons of the cyanobiphenyl group. The compositional analysis was carried out also using UV spectroscopy to get a confirmation of the data obtained by NMR spectroscopy. Poly-(2-N-carbazoylethylmethacrilate) was chosen as a reference compound. This polymer and copolymer **3** show an absorption peak at 342 nm. UV spectra were run for a set of solutions of poly-(2-N-carbazoylethylmethacrilate) in methylene chloride to get a calibration curve plotting absorbance values against percent concentration of the homopolymer.

Then the molar percentage of monomer **1** has been determined from the UV spectra of different kinds of copolymer **3** using the calibration curve and, by difference, the amount of monomer **2** has been derived.

The data, obtained using the two different spectral techniques, are consistent and they both confirm the preference in the addition of monomer **2** with the respect to the addition of monomer **1** in the copolymer. This behaviour can be observed in Figure 1 where the molar percentage of monomer **2** is plotted versus its molar percentage in the feed. The dotted line refers to an ideal behaviour according to which monomer **2** is incorporated in the copolymer in the same proportion as in the feed.

Morphologic Analysis of The PDLC Films

PDLC films were prepared under the same conditions using the mixtures listed in Table 2. The only difference among the mixture is in the composition of the copolymer.

All the samples were investigated by scanning electron microscopy (SEM). In our work a Philips XL 20 SEM operating at 7 kV was used to study the morphology of the samples. A professional Image Analysis Software Package (Image Pro-Plus by Mediacybernetics) was used to perform spatial calibrations of the acquired SEM pictures and statistical analysis of the droplet diameter distributions. All the observed samples show the typical cheese-like morphology of PDLC films with droplet diameters ranging from 0.5 to 3.2 μm .

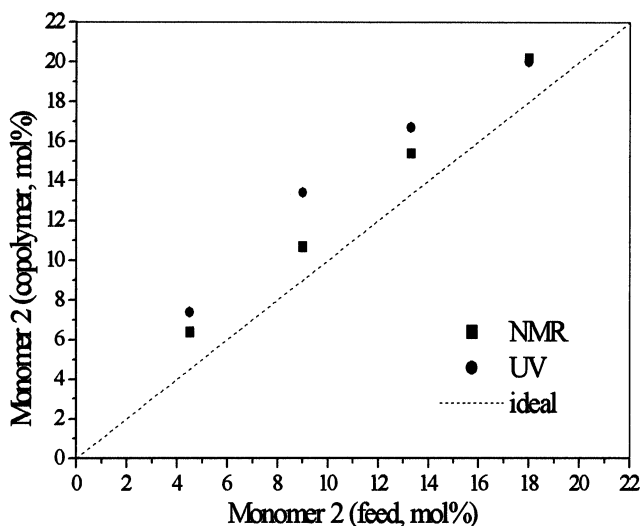


FIGURE 1 Analysis of copolymer composition.

The statistical analysis performed on a large quantity of samples prepared using different mixtures put in evidence that the average domains diameter grows as the amount of monomer **2** in the copolymer **3** gets bigger. This trend is clearly shown in Figure 2 where the mean domains diameter is plotted as a function of monomer **2** molar concentration in the feed. A comparison between sample M1 and sample M5 allows us to do the following considerations. We used poly-(2-N-carbazolyethylmethacrylate) to prepare mixture M1, while we used copolymer C3 to prepare mixture M5. It is then possible to evaluate the effect of the introduction of a monomer with a mesogenic core in the matrix on the morphology of the PDLC films.

SEM micrographs and the respective droplet diameter distributions for samples M1 and M5 are shown in Figure 3.

It has been found that the mean diameter of liquid crystal domains is 1.1 μm for sample M1 and 2.7 μm for sample M5. It is possible to explain this evidence supposing that the mesogenic units in the copolymer form cavities, whose dimensions grow bigger as the concentration of monomer **2** increases. Liquid crystal molecules, considering the similarity among their structure and the one of the mesogenic core present in the copolymer, diffuse in those cavities during phase separation process before polymer gelation occurs.

Moreover, the two distributions shown in Figure 2 clearly prove that the liquid crystal domains number decreases passing from sample M1 to sample M5. The increase of the amount of monomer **2** in the copolymer could lead

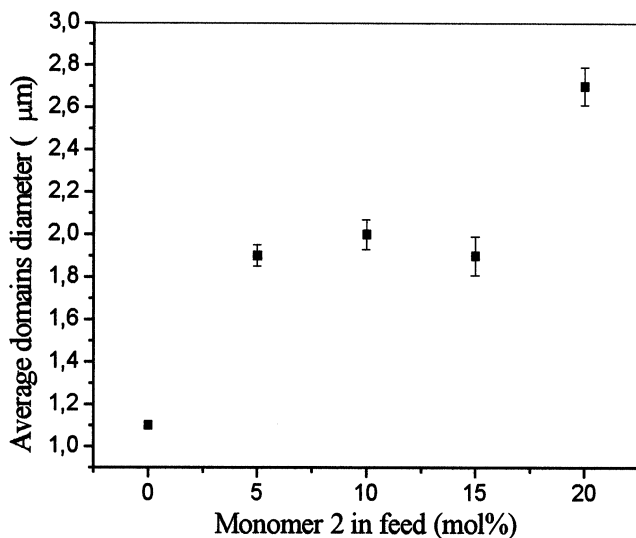


FIGURE 2 Average domains diameter as a function of the concentration of monomer 2 in the feed.

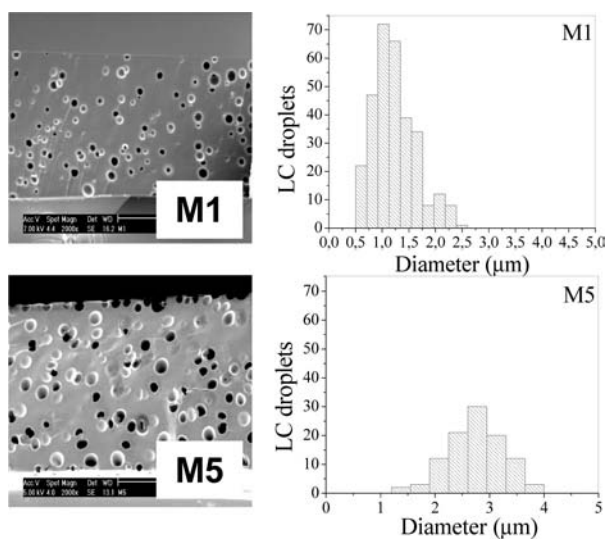


FIGURE 3 SEM micrographs and droplet diameter distribution for samples M1 and M5.

to an higher solubility of the liquid crystal in the polymer matrix, explaining the decrease in domains number.

On the contrary even if the total number of liquid crystal droplets (for an analyzed area of $6400\ \mu\text{m}^2$), is 315 for sample M1 and 108 for sample M5, it was found that the total area of the liquid crystal domains is about $412\ \mu\text{m}^2$ for sample M1 and about $682\ \mu\text{m}^2$ for sample M5. This simply means that the liquid crystal volume fraction separated from the polymeric matrix is higher for sample M5 than for sample M1.

As a consequence it can be stated that the phase separation process is better accomplished increasing the amount of monomer **2** in the copolymer used as matrix in PDLC fabrication.

CONCLUSIONS

In this article we have reported the synthesis and the compositional characterization of a novel polymeric material which shows both photoconductive and mesogenic cores as pendant groups. PDLC films have been prepared using this copolymeric material with the aim of understanding the relationship between the copolymer's composition and the morphology of the obtained PDLC films. A morphological analysis, performed by means of scanning electron microscopy, has clarified the role played by the copolymer composition in controlling the average domains size and in favouring the phase separation process.

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