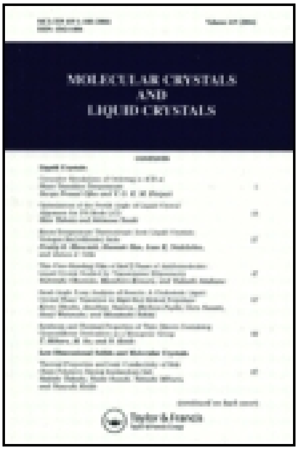

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Stanislaw J. Klosowicz & Józef Żmija (1994): How to Choose the Proper Polymer to PDLC Prepare, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 249:1, 163-169

To link to this article: http://dx.doi.org/10.1080/10587259408038665

Mol. Cryst. Liq. Cryst. 1994, Vol. 249, pp. 163–169
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Printed in the United States of America

HOW TO CHOOSE THE PROPER POLYMER TO PDLC PREPARE

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Abstract Polymer dispersed liquid crystals exhibit some advantages in applications and also interesting physical properties. In this contribution we present general rules of choosing a proper polymer, which fulfill all basic requirements, for PDLC preparation.

1. INTRODUCTION

The base of polymer dispersed liquid crystals (PDLC) technology is preparation the polymer layer which contains droplets of liquid crystal. Different external stimulants (electric, magnetic, thermal, optical or mechanical) may change properties of dispersed liquid crystal phase and, in this way, macroscopic optical properties of PDLC. This stimulation may be controlled -- in this case we can talk about PDLC information displays, or uncontrolled -- this is the case of liquid-crystalline detectors. Of course observed optical effects are slightly different from those known from classic LCD physics, however, electrically driven PDLC may be considered, in spite of all differences, as elastic liquid crystal display. In fact, only few polymers are typically used for PDLC preparation, but possibilities of are much more extensive and depend on designed technology and application. In some applications polymer properties may play the crucial role for proper work of PDLC. In this contribution we present the general rules how to choose the right polymer for PDLC preparation from many well-known polymers.

Till now we have four essential methods of PDLC preparation. They are:

- encapsulation,
- thermally induced phase separation (TIPS),
- solvent induced phase separation (SIPS),
- polymerization induced phase separation (PIPS).

We will not describe these methods here because they are described in details in many papers (for instance,[1] and References therein) but it is obvious that polymers used in each one should have different properties, e.g., solubility, melting point, polymerization mechanism and surface properties.

2. GENERAL PROBLEMS

The first crucial problem is that polymer or prepolymer material should not react with LC material. In some cases a film-forming material, a modifying dopant or a curing agent may react with mesogen. The example is a reaction between polyamine curing agent used for epoxy resins and cholesterol derivatives or benzeneisothiocyanates. Polyamine causes in this case fast degradation of mesogen molecules and so liquid-crystalline properties of the mesogen. The effect of such reaction is an uncontrollable change of liquid crystal parameters, especially a mesophase temperature range and electrooptical properties. The latter involves change of refractive index, dielectric permittivity, elastic constants and so switching voltage, response times and contrast ratio.

A polymer applied for PDLC preparation should be obtainable in form of thin layer and should exhibit good adhesion to boundary surfaces (glass plates or polymer sheets). Surface properties of polymer and, on the second hand, concentration of LC material should lead to formation of LC droplets in polymer matrix. This is so called "Swiss cheese" structure.[2] Despite used preparation method, the miscibility of system components (usually presented in form of phase diagram) should allow eventually to form LC droplets embedded in polymer matrix. In some cases the inverted process may occur; e.g., in case of a mixture of cholesterol esters and methyl methacrylate, polymerization process leads to formation of polymer balls in LC matrix for relatively low LC concentration.[3]

The internal arrangement of cured polymer should ensure sufficiently high concentration of LC droplets because only in this case one may obtain high electrooptical contrast ratio for relatively low layer thickness and, on the second hand, the excess of liquid crystal is not pushed out to a layer surface during curing process. The latter effect may decrease an adhesion of layer to boundary surfaces and complicate the interpretation of electrooptical response due to an existence of two different media (LC and PDLC) with different electrooptical properties.

A polymer should be durable to the thermal, photochemical and chemical degradation. The majority of common polymers fulfill this requirement, at least to more extent than LC materials do. In some cases, however, a small change of polymer properties may play a crucial role, for instance, in case of UV-caused decrease of a polycarbonate transparency. Another example is poly(vinyl alcohol) which may be used for PDLC preparation but it is sensitive to water (in form of vapor, as well). PVA based PDLC should be therefore carefully secured from water penetration.

3. OPTICAL PROPERTIES

Because an optical contrast of PDLC is defined as a quotient of a light transmission in on-state and in off-state, the transmission of visible light by thin (~ 20 μm) layer of pure polymer should be very good, i.e., higher than 95 per cent. This condition practically eliminates polymers exhibiting milky scattering of light. Such a behavior is typical in case of commercial polymers containing a filler. The transmittance of polymer thin layer may be also not satisfactory when polymer is crystalline in high degree. The example is polypropylene which may be obtained in crystalline or amorphous polymer. Used polymers would not absorb a light from visual part of spectrum, as well (i.e., they would not be colored). In the latter case, however, a possibility exists to apply colored polymers for construction of PDLC with color effects.

The second crucial requirement is that the polymer refractive index n_p should be very close to the LC ordinary refractive index n_o, while the mean refractive index of LC should not match n_p at all. We should recall to mind here, that in scattering off-state of the PDLC, the orientation of director inside each droplet is random, while in on-state, when electric field is applied, the director is uniformed and nearly parallel to the direction of electric field vector. Therefore, the goal of this condition is to eliminate the light scattering on the dielectric boundaries between polymer and liquid crystal in on-state and introduce it in off-state. The specific value of n_p depends of course on the properties of used LC material, but usually it should be close to 1.5 (see Table 1). Of course liquid crystals may be as chemical individuals as mixtures.

As one can see, in Table 1 many well-known polymers are not listed, e.g., poly(tetrafluoroethylene) -- $n_p = 1.35$, cellulose acetate -- $n_p = 1.46$ or polyvinylidene chloride $n_p = 1.63$, because of their too small or too large refractive indices. It is of course possible to use appropriate co-polymers with especially adjusted n_p value but an easier way is to adjust n_o value by the change of LC composition. It is worth mentioning that for the majority of common polymers the temperature dependence of

n_p is not very strong (typically about 10^{-4} 1/K) and may be therefore omitted if PDLC is designed to work in temperature range from, say, 250 to 350 Kelvin degrees.

In some cases more complicated adjustment of refractive indices is desired. For instance, if PDLC should be transmittive in off-state and opaque in on-state, the mean refractive index of LC droplets $\bar{n}$ should match n_p and n_0 should differ from n_p as much as possible. Another example is application of ferroelectric smectic S_C* in PDLC, where one should distinguish refractive indices related to director and refractive indices related to helical axis.

Table 1. The comparison between an ordinary refraction coefficient of some common polymers and appropriate liquid crystals.

Liquid crystal	$n_o = n_p$	Polymer
hexylcyclohexane cyanobiphenyl	1.49	poly(methyl methacrylate)
hexylcyclohexane benzeneisothiocyanate	1.52	poly(vinyl butyral) or NOA65 (Norland Optical Adhesives)
pentyl cyanobiphenyl	1.53	polyamide
4-pentyl, 4'-heptyl azoxybenzene	1.55	poly(vinyl chloride)
ZLI-3303 (Merck)	1.58	polystyrene
ZLI 3415 (Merck)	1.59	polycarbonate

4. PHASE TRANSITIONS AND HEAT PROPERTIES

These properties are especially significant when PDLC is prepared by TIPS method. The melting or thermal degradation temperature ranges should excess 370 Kelvin degrees (from application point of view, of course). On the other hand, because the main sense of thermally induced phase separation method leads in use thermoplastics as film-forming polymers, the melting of a polymer should occur in a temperature T_m below temperature of mesogen thermal decomposition because otherwise one cannot control a composition of liquid crystal and so its physical parameters.

The other limitation is that temperature interval, in which PDLC is desired to work, should be above the glassy temperature T_{gl} of a polymer because of sufficient elasticity of PDLC, especially in the case of so called elastic displays. In many applications, however, this limitation may be omitted, e.g., if substrata of PDLC cell are glass plates. In the effect not only elastomers may be used as polymer matrices. Requirements mentioned above eliminate a large number of well-known thermoplastics, but still exists a possibility to adjust of glassy and melting temperatures by doping a polymer by plasticizers, which as a rule decrease these temperatures, typically by 10 to 30 Kelvin degrees.[4] Using low-molecular plasticizers one should remember that some of them can easily dissolve in liquid crystal and change its physical, especially electrooptical parameters. In Table 2 the example is presented of some thermoplastics usable and unusable in TIPS method. Individual values of phase transition temperatures depend on polymer molecular mass. As plasticizers typically alkyl phthalates, alkyl adipates, other esters, polyols and fatty acids are used.

Table 2. The usability of thermoplastics for PDLC preparation from point of view their phase transitions.

Thermoplastic	T_m [K]	T_{gl} [K]	PDLC usability
Poly(methyl methacrylate)	385-393	460	yes
Polyamide 6,6	243-248	527	no
Polyethylene	148-248	375-410	yes
Polypropylene	250-255	433-450	yes
Poly(vinyl chloride)	348-378	423-493	yes
Poly(ethylene terephtalate)	345	533	no
Polycarbonate	414-422	493-503	no
Poly(vinylbutyral)	330	422	yes

If polymer is obtained in the process of chemical or photochemical curing of prepolymer a polymerization is preferred rather than polycondensation, because in the latter case, low-molecular products of reaction may cause an arising of bubbles in prepared system. Such bubbles may be removed from the system by slowly made curing.

5. SURFACE PROPERTIES

The essential problem to make a PDLC display or even to study electrooptical properties of PDLC, is a good adhesion of PDLC layer to the surfaces with conducting layer. They may be glass plates or polymer sheets. The filling of a cell in the first case and the laminating process in the second one should lead to the obtain a stable structure without tendency to layer separation. It can be improved by special treatment of base surfaces but the main sources of a failing remain too large surface tension of a polymer in liquid phase, poor adhesion to substrata's material and the presence of liquid crystal on a phase boundary. As we have mentioned above, surface properties of polymer should allow to form LC droplets in polymer matrix but no vice versa.

6. SUMMARY

Taking into account above mentioned requirements and polymer properties one can select the most promising polymers for PDLC preparation. They are presented in Table 3. Of course it touches upon the most widespread individual polymers (with the exception of the last material). On the other hand, this list is not closed and many more polymers may be probably used for PDLC preparation, especially for particular purposes, but still on the base of general requirements.

The possibility of application of appropriate co-polymers with designed properties still exists and may be very interesting. Authors hope that material engineering will improve properties of existing polymers or even develop new materials, soon.

ACKNOWLEDGEMENT

This work was supported by Committee of Scientific Research Grant no. 7.7370.91.02.

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Table 3. The most promising polymers for PDLC preparation.

Polymer	PDLC preparation	Surface properties	Stability	Comments
Poly(vinyl butyrate)	TIPS	very good	good	displays, switchable windows
Poly(ethylene) (amorphous)	TIPS	good	very good	
Poly(methyl metacrylate)	TIPS, SIPS, PIPS	mean	good	
Poly(vinyl cyclohexanal)	TIPS	good	good	displays
Epoxy resins	TIPS, PIPS (UV)	very good	very good	all applications
Poly(vinyl alcohol)	encapsulation	mean	mean	detectors, switchable windows
Polystyrene	SIPS	mean	good	
Latex	encapsulation	mean	mean	detectors