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(6) We start from the equation

$$\Delta\phi = 2bl\sigma - abl\Delta G + \lambda kT \ln (l_o/x_o) - (\nu - 1)ab(l\Delta G - 2\sigma_e) \quad (3)$$

The condition $\Delta\phi = 0$ with $l = l_g^* = l_c + \delta$ where $l_c = 2\sigma_e/\Delta G$ (6) and $\delta = kT/2b\sigma$ gives

$$L_t > (\sigma/\sigma_e)l_c^2/\delta + (\sigma/\sigma_e)l_c - (a/\delta)l_c \quad (4)$$

The sign ">" occurs because, in the right-hand side of this inequality, we have omitted the third term of the right-hand side of the equation (3) (because the exact values of x_o and λ are not given in ref 1). The lower bounds of L_t for representative PE fractions studied by Hoffman et al.[2] are the following. For the fraction of $M_W = 18\,100$, $n_z = 2000$, it varies from 33.1 to 78.2 nm when the crystallization temperature t goes from 122.5 to 129 °C. For the fraction $M_W = 30\,600$, $n_z = 2740$, it varies from 34.4 to 82.6 nm when t goes from 124 to 130.5 °C. For the fraction $M_W = 74\,400$, $n_z = 6130$, it varies from 25.0 to 75.7 nm when t goes from 122 to 131 °C. Thus the inequality $L_t > L$ is obtained from the HM theory in each experimental condition used by Hoffman et al. in their classical work,[2] which is considered as the foundation of the HL theory. See also: Hoffman, J. D.; Davis, G. T.; Lauritzen, J. I., Jr. In *Treatise on Solid State Chemistry*; Hannay, N. B., Ed.; Plenum: New York, Vol. 3, Chapter 7, or any textbook on polymer physical chemistry.

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(8) We have other remarks on the HM paper concerning the use of the reptation concept, the sharpness of the observed "regime transition", and the assumed shape of the molecules in the nuclei. However, we think that it is more appropriate, in this paper, to concentrate our attention on the inequality (2).

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(10) It may be that this disagreement does not occur when crystals grown from solution are concerned. Nevertheless, we show elsewhere[15] that the HL theories cannot explain the kinetics of crystallization of LPE single crystals grown from solution.

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Response to Criticism of Nucleation Theory As Applied to Crystallization of Lamellar Polymers

In the preceding paper, Point and Dosière[1] (hereafter P&D) criticize a widely used body of theory concerning crystallization of lamellar polymers because of a supposed major inconsistency involving the magnitude of the substrate length L and because they apparently do not accept experimental evidence concerning the reality of regime transitions in such polymers. Regarding the latter, they state "Finally, we seriously question the existence of regime transitions". This refers specifically to the regime I → II transition. The theoretical framework they challenge is that commonly termed "LH" or "HL", which is based on the work of Lauritzen and Hoffman[2] as extended to include the prediction of regime I → II transitions[3-5] (involving the introduction of a finite substrate length L), regime II → III transitions,[6,7] the effect of reptation,[8] and recently an improved version of the latter by Hoffman and Miller (HM)[9] that included a rough estimate of L for melt-crystallized polyethylene. It is this estimate of L that constitutes part of their objection. Evidently P&D consider regime I to be "completely hypothetical", which if correct would leave no room for believing in the reality of a I → II transition, let alone the presence of a substrate of length L to explain it. To counter the views of P&D, we first cite experimental results showing that regime transitions do occur and then deal with their criticism of the magnitude of L.

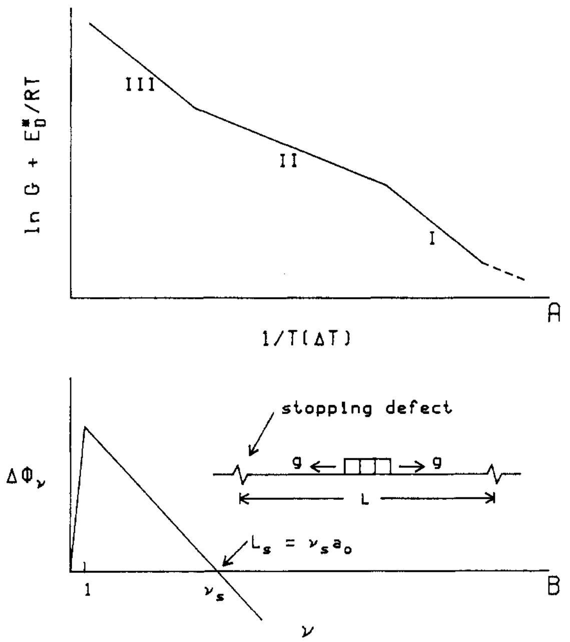

Figure 1. (A) Method of detecting regime transitions. The dashed line indicates a reversion to regime II that may occur at high temperatures (see ref 25). For bulk rate data, ln G is replaced by ln (τ_χ^{-1}). (B) Barrier system for HL–HM models. Inset shows schematic representation of substrate length L. The quantity g is the substrate completion rate.

A. Are Regime Transitions Real? For crystallization of lamellar polymers with chain folding, nucleation theory predicts the presence of three regimes denoted I–III.[3-7,9] To detect them, one commonly plots $\ln G + E_D^*/RT$ vs $1/T(\Delta T)$ as shown schematically in Figure 1A. Here G is the observed lineal growth rate, T the isothermal crystallization temperature, ΔT the undercooling, and E_D^* the activation energy of transport of molecules to the crystal interface.[10] Where the bulk crystallization rates are employed, one plots $\ln (\tau_\chi^{-1}) + E_D^*/RT$ vs $1/T(\Delta T)$ where τ_χ is the time required to attain a fixed degree of crystallization χ. The slope changes in Figure 1A signify the presence of regime transitions. As one goes from regime I to regime II, the slope is predicted to fall by a factor[3-5] of 2, and as one goes from regime II to regime III, the slope is predicted to increase by a factor[6] of 2. Polymer systems showing *experimentally* such slope changes are listed in Table I and discussed more fully below. We quote only those examples where the author(s) stated that the I →

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Table I
Regime Transitions in Various Polymers

polymer	author(s)	method[a]	remarks
	A. Regime I → II Transitions		
polyethylene	Hoffman, Lauritzen, Ross, and Frolen (1975)[3,9]	A	melt crystallization, 11 fractions
polyethylene	Allen and Mandelkern (1987)[12] (data of ref 13)	B	melt crystallization
polyethylene	Organ and Keller (1986)[11]	A	dilute solution (tetradecanol and hexadecane)
poly(L-lactic acid)	Vasanthakumari and Pennings (1983)[14]	A	melt crystallization, 1 fraction only
poly(1-3 dioxolane)	Alamo, Fatou, and Guzman (1982)[15]	A	melt crystallization
cis-poly(isoprene)[b]	Phillips and Vantansever (1987)[16]	A	melt crystallization
poly(dimethylthietane)[b]	Lazcano, Fatou, Marco, and Bello (1988)[17]	B	melt crystallization
poly(ethylene oxide)[b,c]	Cheng, Chen, and Janimak (1989)[18]	A	melt crystallization
	B. Regime II → III Transitions		
polyethylene	Hoffman (1983)[6] (data of ref 19)	A	melt crystallization
poly(oxymethylene)	Hoffman (1983)[6] (data of ref 20)	A	melt crystallization
polypropylene	Clark and Hoffman (1984)[7] (numerous data sets[7])	A	melt crystallization
poly(3-hydroxybutyrate)	Barham, Keller, Otun, and Holmes (1984)[21]	A	melt crystallization
poly(phenylene sulfide)	Lovinger, Davis, and Padden (1985)[22]	A	melt crystallization
poly(pivalolactone)	Roitman, Marand, Miller, and Hoffman (1989)[23]	A	melt crystallization
cis-poly(isoprene)[b]	Phillips and Vantansever (1987)[16]	A	melt crystallization
poly(dimethylthietane)[b]	Lazcano, Fatou, Marco, and Bello (1988)[17]	B	melt crystallization
poly(ethylene oxide)[b,c]	Cheng, Chen, and Janimak (1989)[18]	A	melt crystallization

[a] Method A: $\ln G + E_D^*/RT$ vs $1/T\,(\Delta T)$ plot. Method B: $\ln(\tau_x^{-1}) + E_D^*/RT$ vs $1/T\,(\Delta T)$ plot. [b] Note that these polymers are stated to exhibit both the I → II and II → III transitions in the same sample. [c] The changes of slope at the transitions in this polymer are somewhat abnormal as currently analyzed. Note: the table is restricted to polymers where chain folding occurs; transitions in extended-chain systems are not included.

II or II → III transitions appeared in the data presented or cited.

(i) The I → II Transition. Most of the examples in Table IA deal with crystallization from the melt; note however that a I → II transition has been found[11] for the {110} faces of polyethylene single crystals formed from dilute solution (analyzed with the HL formulation; slope change ~ 2). Note also that the I → II transition in melt-crystallized polyethylene has been found by the bulk rate method.[12] The fact that P&D mention a few I → II transitions, yet question their existence, bespeaks a certain ambivalence in their position. In any case they appear to us to deem it a failing of nucleation theory that the I → II transition is not found in *all* lamellar polymers. That this transition has not been seen in some polymers may result from the fact that growth rate measurements are not practical at the required high temperatures (where such rates can be exceedingly slow). There is in addition good reason to expect regime II to dominate virtually the entire practical range of observable growth in certain systems.[24] Nucleation theory cannot be condemned simply because a I → II transition has *not* been detected in a particular system.

On the basis of Table IA, we firmly maintain that the regime I → II transition does indeed exist in a number of polymers. The case for polyethylene, both melt- and solution-crystallized, seems beyond doubt. This is of importance since it is the HM estimate[9] of L for this polymer that P&D have placed at issue (see later). For melt-crystallized polyethylene, the I → II transition can be seen unmistakably in plots of log G vs T.[3,5] This is also true in some other cases. The slope change at the I → II transition in the type of plot depicted in Figure 1A is usually fairly close to the predicted factor of 2.

(ii) Regime II → III Transitions. We give in Table IB those polymers that exhibit an unmistakable II → III transition. We are justified in including these by the fact that the II → III transition arises from the same basic nucleation model, though here L is not involved. In most cases the slope change is close to the predicted factor of 2. The reality of numerous II → III transitions is proved beyond doubt.

(iii) Polymers with both I → II and II → III Transitions. Observe that three of the polymers in Table I, namely *cis*-poly(isoprene),[16] poly(dimethylthietane),[17] and poly(ethylene oxide),[18] exhibit *both* the I → II and II → III transitions *in the same sample.* Plots of $\ln G$ (or $\ln \tau_x^{-1}$) + E_D^*/RT vs $1/T(\Delta T)$ for these polymers bear a striking resemblance to the totality of Figure 1A.[25] For *cis*-poly(isoprene) and poly(ethylene oxide), the ratios of slopes in the plots showing both the I → II and II → III transitions are sensitive to choice of U^* and T_∞ in $E_D^*/RT = U^*/R(T - T_\infty)$.

(iv) Summary. The statement of P&D that "we seriously question the existence of regime transitions" is itself to be questioned, implying as it does the omission from consideration of a large body of experimental evidence to the contrary. Regime I → II and II → III transitions are real and usually conform to theoretical expectations. P&D offer no credible alternative to a regime transition to explain the behavior listed in Table I and depicted schematically in Figure 1A. Whatever blemishes the HL–HM approach may still retain, the prediction of the I → II and II → III regime transitions is not one of them: When these transitions are sought after by determined and competent investigators, they are frequently found (Table I).

B. Is the Estimated Value of L for Melt-Crystallized Polyethylene Inconsistent with the Size of a Stable Surface Nucleus? The presence of a I → II effect implies the existence of a finite substrate length L, which is essential to the prediction of the transition. We take L to be the mean distance between "stopping" defects on the substrate.[9] P&D assert that the value of L estimated by HM for melt-crystallized polyethylene is too small to be credible because it is considerably less than the length L_s of a stable nucleus. Here again P&D question the regime I → II transition concept, including the existence of regime I. The barrier system showing the meaning of L_s is shown schematically in Figure 1B. (P&D denote L_s by the symbol L_t; our L is their L or L(1).) The P&D argument is based on an arbitrary selection of a sometimes inapplicable expression for δ, the omission to note another expression for δ given explicitly in HM[9] and earlier papers,[3-8] and a failure to note the error limits that we necessarily place on our estimate of L. Their objection cannot be sustained as a general case.

The HM estimate[9] of the magnitude of L from kinetic data depends directly on the ratio Z_I/Z_{II}^2 where Z_I and Z_{II}

Table II
Comparison of L and L_s for Melt-Crystallized Polyethylene Fractions at Various Undercoolings: HL–HM Theory Valid When $L \simeq L_s$ or $L > L_s$

	δ, Å	L, Å	L_s,[a] Å	remarks
A. At Highest T_x in Regime I ($\Delta T \simeq 13$ K, $T_x = 403.7$ K)				
eq 2	5.69	~500 (assumed)	894	contradiction evident: eq 2 probably not valid at this low ΔT (see text)
eq 3	11.37	~500 (assumed)	460	theory valid
LP	24[b]	~500 (assumed)	232	theory valid
B. At Regime I → II Transition ($\Delta T = 16.5$ K, $T_x = 400.2$ K)				
eq 2	5.64	~500	548	contradiction marginal
eq 3	11.28	~500	284	theory valid
LP	27[b]	~500	131	theory valid
C. At Low T_x in Regime II ($\Delta T = 20$ K, $T_x = 396.7$ K)				
eq 2	5.59	~500 (assumed)	364	theory valid
eq 3	11.18	~500 (assumed)	191	theory valid
LP	30[b]	~500 (assumed)	82	theory valid

[a] Calculated by means of eq 1. For the case of melt-crystallized polyethylene, a_0 (stem width) = 0.455 nm, b_0 (layer thickness) = 0.415 nm, Δh_f (heat of fusion) = 2.80×10^9 erg cm^{-3}, σ (lateral surface free energy) = 11.81 erg cm^{-2}, σ_e (fold surface free energy) = 90 erg cm^{-2}, and x_0 (length of statistical chain unit) = $l_u \times 6.7$ = 0.853 nm, and for the term involving λ, we use $\lambda = {}^1/_3$ corresponding to an angle of sweep[9] of a cilium of 270°. The calculations in the table apply to a sample with $M_w = 30\,000$ for which T_m = 416.7 K and l_0 (length of chain) = 272.3 nm. For approximate calculations one may use the working expression L_s (Å) = $9.418 \times 10^5/\delta$ (Å)$(\Delta T)^2 + 351.6/\Delta T - 8.380 \times 10^3/\delta$ (Å)ΔT exact at the I → II transition and adequate at other temperatures. The case considered by P&D ($M_w = 115\,000$, $T_m = 418.1$ K) gives similar results. [b] Values of δ estimated from LP fluctuation theory[29] as adjusted to $\sigma = 11.8$ erg cm^{-2} (average for $\Psi = 0$ and $\Psi = {}^1/_2$).

are the experimentally determined preexponential factors for the growth rate in regimes I and II. In the past, order of magnitude accuracy for the values of the Z's would have been considered exceptional! Even with growth rate data on 11 fractions and an improved (HM) theory, we still have been able to attain only limited accuracy for the value of Z_I/Z_{II}^2. We stated in ref 9 that "$L \simeq 210$ Å *within a factor of about 2*". Our recent assessment[26] would assign an error of a factor of about 3, which many will recognize as still remarkable. Here we employ the estimate $L \simeq 500$ Å, which is well within the revised error limit and not forbidden by the original limits. This estimate holds specifically at the I → II transition, which occurs[9] at $\Delta T_{I\to II} = 16.46 \pm 0.36$ K in melt-crystallized fractions;[27] this is the only point at which L may be evaluated directly. In Table II we assume that L is similar at the other undercoolings. With $L \sim 500$ Å, one does not expect nonlineal growth effects in any but exceedingly small crystallites.[27]

To find the value of L_s, one begins with the free energy of formation of a surface strip possessing ν stems.[9] Then, employing[2-9] $l = l_g^* = 2\sigma_e/(\Delta G) + \delta$ and setting $\Delta\phi_\nu = 0$, one gets for the number of stems in the stable nucleus

$$\nu_s = \frac{4\sigma\sigma_e}{a_0\delta(\Delta G)^2} + \frac{2}{\Delta G}\left[\frac{\sigma}{a_0} - \frac{\sigma_e}{\delta}\right] + \frac{\lambda kT \ln (l_0/x_0)}{a_0 b_0 \delta(\Delta G)} \tag{1}$$

in which, to a sufficient approximation, we may use $\Delta G = \Delta h_f(\Delta T)/T_m$. The stable nucleus length is given by $L_s = \nu_s a_0$ (Figure 1B). The term in λ in eq 1 results from the free energy of attachment of the first chain.[9] Symbols and their values are identified in Table II.

In the paper by HM[9] *two* expressions were given for δ, which depended on whether the backward reaction for stem addition was active or not. The one extreme of an inactive backward reaction (thought to be relevant at relatively large ΔT) yielded[9]

$$\delta = kT/2b_0\sigma \tag{2}$$

This is the only δ referred to by P&D. For the conventional case where the backward reaction is fully active (taken to be valid at relatively low ΔT), HM gave the result characteristic of many[3,5-9,28] HL papers

$$\delta = \frac{kT}{2b_0\sigma}\left[\frac{(4\sigma/a_0) + \Delta G}{(2\sigma/a_0) + \Delta G}\right] \cong kT/b_0\sigma \tag{3}$$

For the HL–HM approach to be self-consistent one needs either of the conditions $L \simeq L_s$ or $L > L_s$. We list in Table II results for L_s as calculated with eq 1 and the two expressions for δ (eq 2 and 3) at various practically attainable undercoolings.

The first point to notice is that the case $\delta \cong kT/b_0\sigma$ (eq 3) leads to no anomaly. Here L is always greater than L_s, as required for the theory to be consistent. P&D did not consider this case, even though eq 3 is widely known and moreover was explicitly given in HM.[9]

Where the backward reaction is muted, δ is given by eq 2 and there is a difficulty in regime I at the highest T_x corresponding to $\Delta T \cong 13$ K. The problem is marginal at the I → II transition at $\Delta T = 16.5$ K and not present at all at low T_x. The problem with eq 2 at the high T_x could have been anticipated, since in HM and elsewhere[26] we noted that the backward reaction would be expected to become more active there, leading to $\delta \to kT/b_0\sigma$ and thus $L \simeq L_s$. Even so, the $\delta = kT/2b_0\sigma$ version does not present a problem in the main portion of regime II.

For completeness, we include in Table II calculations of L_s based on the δ values estimated from the nucleation-based theory of Lauritzen and Passaglia[29] (LP) in which fluctuations of fold period are permitted. The LP theory, which is in the general spirit of the HL formulation, leads to an expression for the initial lamellar thickness l_g^* of the usual form, but with a larger δ than that of HL. This advanced form of nucleation theory gives values of δ, which *everywhere* in Table II lead to the required condition $L > L_s$.

Summary. A reasonable estimate of L, taken together with the use of the most relevant formulae for δ in calculating L_s, leads to realistic situations where $L \simeq L_s$ or $L > L_s$ for melt-crystallized polyethylene as Table II shows. The proposal that the HL–HM formulation is generally invalid in this case because $L < L_s$ cannot be sustained; the assertion by P&D that the HL–HM type of theory is not self-consistent is assuredly not generally correct. Moreover, the magnitude of L is such that regime I can exist, allowing both regime I and L to be regarded as physically real properties that are worthy of further study.[30]

Registry No. Polyethylene, 9002-88-4.

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Macromolecules **1989**, *22*, 3505–3506

(10) It is essential to have an accurate value of the dissolution temperature $T_d°$ or the melting point T_m in making plots of $\ln G + E_D^*/RT$ vs $1/T(\Delta T)$ since otherwise distortions (missed transition or a spurious transition) can result. This is especially true of the I → II transition. In crystallization from the melt at low undercoolings, E_D^* may be identified with Q_D^*, the activation energy of reptation.[8,9] When the undercooling range is large, one uses $E_D^*/RT \rightarrow U^*/R(T - T_\infty)$. In constructing Table I we have omitted reports of transitions where we had reason to suspect significant errors in T_m or $T_d°$.

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(24) Polymers with a restricted configurational path degeneracy tend to exhibit a large range of regime II behavior (see, e.g., ref 9). Isotactic poly(styrene) evidently behaves in this manner.[5] In some cases, regime I may be entirely absent (see ref 25).

(25) In the cases of *cis*-poly(isoprene) and poly(ethylene oxide) the growth rate data suggest a reversion to regime II behavior at temperatures above regime I. This possibility was anticipated prior to its observation: the defects that define L may anneal away or have a short lifetime at high T_x. See: Hoffman, J. D. *Polymer* **1985**, *26*, 1763. If the defects should be especially labile, regime I might not occur at all.

(26) Hoffman, J. D.; Miller, R. L. *Macromolecules*, in press.

(27) Because the undercooling at which the I → II transition occurs in *n*-tetradecanol and *n*-hexadecane is larger[11] than it is for melt-crystallized polyethylene ($\Delta T \cong 16.5$ °C), L should be smaller for the solution-grown crystals.

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(30) P&D evidently believe that all HL–HM developments involve a stem that goes down on the substrate in a single step. The reader should be aware that, in recent versions of the theory, a stem does not add in a single step (e.g., as a rigid rod) but instead goes through a definite "partial stem" stage for the realistic case where Ψ is less than unity (see ref 26).

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Photochemical Alignment Regulation of a Nematic Liquid Crystal by Langmuir–Blodgett Layers of Azobenzene Polymers as "Command Surfaces"[1]

The nature of substrate surface plays an essential role in liquid-crystal (LC) alignment.[2] Recent investigations in our group have revealed that parallel ⇌ homeotropic reversible alignment mode changes of a nematic liquid crystal are induced by the cis ⇌ trans photochromic reaction of azobenzene (Az) layers attached on the cell substrates.[3,4] This phenomenon involves alignment changes of ca. 10^4 liquid-crystal molecules commanded by only a couple of Az units on the surface, and in this sense we proposed to refer to these photochromic surfaces as "command surfaces".[3] In this communication we demonstrate that (i) alignment changes are induced by Langmuir–Blodgett (LB) mono- and multilayers of amphiphilic polymers containing Az units, (ii) these molecularly controlled Az layers favorably give detailed information on the conditions for the LC response, and (iii) understanding the present phenomenon demands the knowledge of orienting mechanisms on a molecular level at the LC/photochromic layer interface.

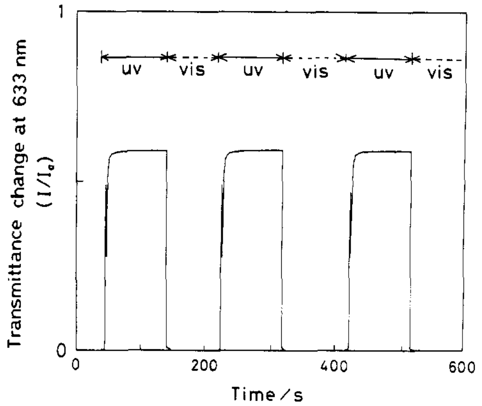
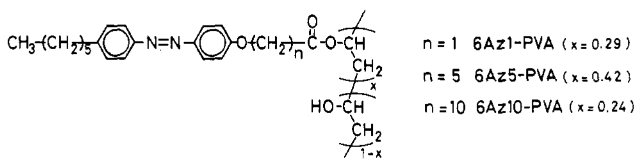


Figure 1. Reversible transmittance change of He–Ne laser light (633 nm) through a LC cell constructed with two glass plates covered with the 6Az10-PVA LB monolayer and polarizers upon alternate exposure of UV and visible light. I and I_0 indicate the laser beam intensities passed through two crossed polarizers with an LC cell and two parallel polarizers without an LC cell, respectively. UV (366 nm) and visible (436 nm) light irradiations were performed using a 500-W super-high-pressure mercury lamp and appropriate combinations of Corning glass filters.

LB mono- and multilayers on glass substrates were prepared from poly(vinyl alcohol) having Az side chains (6Az*n*-PVA).[5] These polymer-type amphiphiles were required to obtain photoreactive Az–LB films.[6] Az–LB films composed of simple amphiphiles such as carboxylic acid derivatives were not applicable for the present purpose because of their poor photoreactivity.[7] 6Az*n*-PVA was spread from a 1 × 10^{-3} mol dm^{-3} chloroform solution on a Langmuir trough (Lauda film balance) filled with doubly distilled water at 21 ± 0.5 °C. 6Az*n*-PVA in chloroform was previously converted to the cis form (≅90%) upon UV light irradiation before spreading on the subphase, and the monolayers were deposited onto glass plates at good transfer ratios (>0.9). This *cis*-Az deposition was adopted throughout the experiments because the films obtained in this procedure gave the higher cis conversion than *trans*-Az deposited ones.[6] Film preparations were achieved under safe light. A nematic liquid crystal 1 (DON 103, C-17-N-73-I, Dainippon Ink & Chemicals Inc.) mixed with 8-μm glass spacer was sandwiched between two glass substrates modified with the LB films. Alignment changes of the liquid crystal was observed with the transmitting He–Ne laser light (633 nm) through the cell set between two crossed polarizers as previously described.[3,4]



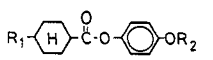


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Figure 1 shows the transmittance changes of 633-nm light through the monolayered 6Az10-PVA/liquid-crystal

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