Polymer–Polymer Composites Fabricated by the *In Situ* Release and Coalescence of Polymer Chains from Their Inclusion Compounds with Urea into a Carrier Polymer Phase

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ABSTRACT: Inclusion compounds (ICs) can be formed between small-molecule hosts and guest polymers, where the crystalline host lattice confines the guest polymers to occupy narrow cylindrical channels. The included polymers are highly extended by the narrow channel diameters and are separated from neighboring polymer chains by the walls of the small-molecule host lattice. It is possible to coalesce the polymer chains from their ICs by exposure to a solvent for the small-molecule host which is not a solvent for the included polymer chains. When crystallizable polymers are coalesced from their ICs by solvent treatment, they are observed to crystallize in an extended-chain morphology accompanied by much less chain-folding than occurs when crystallization of the same polymers take place from their disordered melt or solution environments. In this report we outline our initial efforts to create polymer–polymer molecular composites based on the coalescence of polymer chains from their IC crystals with urea, which were previously embedded in a carrier polymer phase. Both film and fiber composites made with chemically identical or distinct IC-included and carrier polymers are described. Water vapor permeation, differential scanning calorimetry (DSC) and microscopic observations are used to probe these composites; and several applications are suggested. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 281–287, 1997

Key words: polymer inclusion compounds; polymer–polymer composites

INTRODUCTION

A number of small molecules can function as hosts for a variety of guest polymers and form inclusion compounds (ICs) during their cocrystallization, both from solution and the melt. Urea, thiourea, perhydrotriphenylene, cyclotriphosphazenes, and cyclodextrins, for example,[1–4] form ICs with a variety of polymers. In each of these polymer-ICs the small-molecule host forms a crystalline lattice containing narrow parallel channels

where the highly extended guest polymer chains reside. Figure 1 presents views parallel and perpendicular to the channel directions for the polyethylene-urea and *trans*-1,4-polybutadiene-perhydrotriphenylene-ICs, respectively, as determined from single crystal X-ray diffraction analyses.[5,6] As can be seen in these polymer-IC examples, the included polymer chains are highly extended as a consequence of the narrow cross section of the host channels, and polymer chains in neighboring channels are prevented from directly interacting by the channel walls which separate neighboring host channels. For these reasons, we have been forming and studying a variety of polymer-urea-ICs[7–17] and comparing the behaviors of the IC-included polymer chains to

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the behaviors of the same polymer chains in their bulk ordered phases. In this way we obtain some measure of the relative contributions made by the inherent nature of a confined polymer and the cooperative interchain interactions to the conformational and motional behavior of ordered bulk polymers.

In addition, it has been observed that when polymer-ICs are treated with a solvent for the host lattice, which is not a solvent for the guest polymer, the host lattice is dissolved away; and the insoluble guest polymer chains are forced to coalesce and precipitate. More importantly, the coalesced polymer is observed to crystallize without chain-folding as indicated by elevated melting temperatures and an absence of lamellar periodicities as probed by SAXS.[4,10,18] As an example, Figure 2 presents the DSC scans of poly(ϵ-caprolactone) (PCL) crystallized from solution, from the melt, and by coalescence from its urea-IC. Note the 6°C elevation in the melting temperature of the coalesced sample, in comparison to the samples crystallized from disordered solution and melt phases. These observations suggest the use
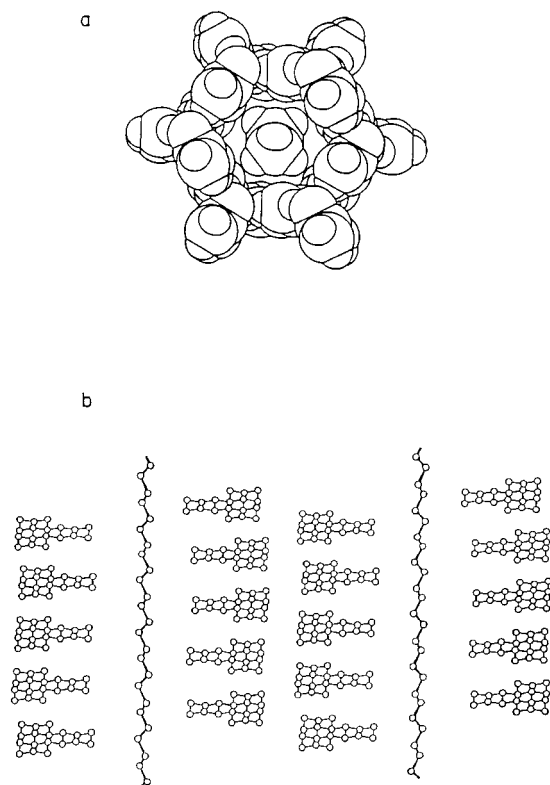
Figure 1 (a) View down the channel of the *n*-hexadecane-urea-IC crystal;[5] (b) View perpendicular to the channel of the polybutadiene-perhydrotriphenylene-IC crystal.[6]
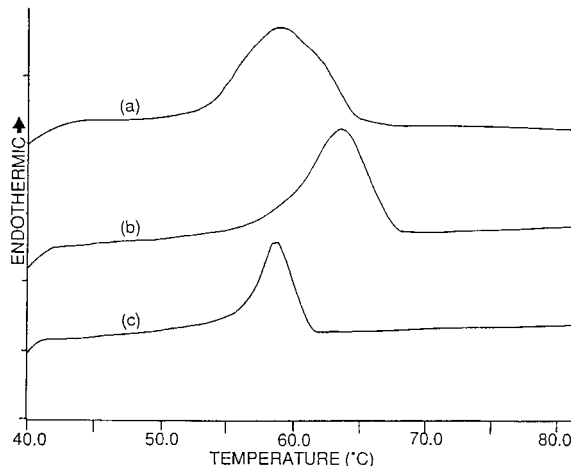
Figure 2 DSC thermograms of PCL: (a) crystallized from solution, (b) coalesced from PCL-urea-IC with methanol, and (c) recrystallized from the melt.[10]

of polymer-ICs to obtain samples with chain-extended morphologies via coalescence of the highly extended, included chains, which apparently is achieved without conformational disordering.

In the present report we present some preliminary results of our attempts to prepare polymer–polymer composite samples by the process of embedding polymer-IC crystals into the fibers and films of a carrier polymer as they are formed, followed by the *in situ* coalescence of the IC-included polymer into the carrier polymer matrix.[19] Most of the results are for fibers and films made with PCL as both carrier and urea-IC polymer, though one example of a heteropolymer composite made with poly(L-lactic acid) (PLLA) carrier and PCL-urea-IC is also described. Microscopic, DSC, and vapor transport observations are utilized to characterize the composite films, and several potential applications are suggested for polymer–polymer composites obtained by embedding polymer-ICs into a carrier polymer matrix, followed by coalescence of the IC-included polymer chains.

EXPERIMENTAL

PCL (MW = 30,000) and PLLA (MW = 285,000)[11] were obtained from Aldrich and from Research Triangle Institute, respectively. PCL-urea-IC was prepared as described previously[7] and embedded into PCL fibers and films as they were melt-processed. This is possible because PCL and PCL-urea-IC melt at 58° and 142°C, respectively. On the other hand, PLLA melts at ca. 180°C, so PCL-urea-IC was embedded in PLLA films cast from

chloroform solutions. Films of PCL and PCL embedded with PCL-urea-IC were also cast from acetone solutions. Film thicknesses were obtained with a Thwing-Albert thickness tester (Model II), and a Perkin-Elmer DSC-7 was employed to obtain calorimetric scans at 10°C/min. Rates of water permeation through the films were obtained from weight loss measurements of pans containing water that were covered and sealed with the films (ASTM E96-80). Coalescence of the PCL chains from PCL-urea-IC into the carrier matrix polymer was achieved by dipping the IC-embedded films overnight in methanol.

RESULTS AND DISCUSSION

Micrographs of the film samples embedded with PCL-urea-IC both prior to and after dipping in methanol are presented in Figure 3. The PCL-urea-IC domains are ca. 50–200 μm in size, and then remain or increase from this size after the PCL chains are coalesced from the urea-IC during the methanol dip. This is not expected since the molar ratio of urea/PCL repeat units is 4/1 or 2/1 (g/g), in PCL-urea-IC,[7,9] so we rather expected the domain sizes to decrease.

Figures 4 and 5 present the DSC scans of the PCL-urea-IC embedded films of PCL and PLLA, respectively, both before and after coalescence by dipping. It is clear from the presence or absence of PCL-urea-IC melting endotherms at ca. 141°C in the films prior or subsequent to methanol dipping, that the dipping process effectively breaks up the IC crystals and removes the urea. It is also apparent that the morphology of the PCL film after coalescence of additional PCL from the urea-IC is altered from that of the IC-embedded, melt-pressed film before methanol dipping. Before coalescence, the carrier PCL melts predominantly at 63°C, implying a chain-extended morphology (see Figure 2); while, after dipping, we observe both chain-extended (61°C) and chain-folded (57°C) melting. During the second heating of both samples, which follows their recrystallization from the disordered melt, it appears that only chain-folded crystals are present. Another interesting feature seen in the first heating scan of the PCL-urea-IC embedded PCL film is that nearly all of the carrier PCL has been induced to crystallize in the chain-extended morphology even though no PCL has been released from the IC crystals. In fact, though not shown here, a melt-pressed film of PCL and urea powder also indicates a chain-extended crystalline morphology for

the PCL carrier apparently nucleated by the tetragonal urea crystals. For the solution-cast film embedded with PCL-urea-IC, the PCL chains melt at 60° and 62°C before and after dipping in methanol, indicating that coalescence of PCL chains from the PCL-urea-IC crystals is, in this case, producing a chain-extended crystalline morphology.

The DSC scans recorded for PLLA solution-cast films embedded with PCL-urea-IC before and after dipping in methanol (Figure 5) show a 5°C increase in PLLA melting, but no melting endotherm is seen for PCL in the dipped film. The endotherm at 134°C observed for the PLLA solution-cast film embedded with PCL-urea-IC is more suggestive of the melting of free, tetragonal urea rather than PCL-urea-IC crystals as seen in Figure 4. Taken together, the DSC scans seem to suggest that during the casting of PLLA films embedded with PCL-urea-IC, the PCL-urea-IC crystals are disrupted and either the released PCL chains no longer reside in the PLLA film; or, if they do, they are not crystalline. In our subsequent discussion of film permeabilities, we will suggest that PCL chains do remain in the PLLA films, but without crystallizing.

Figure 6 presents the DSC scans of PCL fibers spun from pure PCL and from mixtures of PCL and PCL-urea-IC powders. Each fiber was spun at 80°C, a temperature above and below the melting points of PCL and PCL-urea-IC, respectively. Note that the presence of PCL-U-IC seems to induce the chain-extended crystallization of the PCL chains ($T_m = 63°C$), while the pure PCL fiber has crystallized in the normal chain-folded morphology ($T_m = 58°C$). The higher temperature endotherms seen in the PCL-U-IC embedded PCL fibers are more characteristic of free urea ($T_m = 134°C$) than PCL-urea-IC, so the PCL-urea-IC crystals may have been disrupted during fiber spinning.

Table I shows a compilation of film thicknesses and moisture vapor transports through PCL and PLLA solution-cast films with and without embedded urea or PCL-urea-IC crystals, both before and after dipping in methanol. Note that the PCL films seem significantly more permeable to water vapor than the PLLA films; however, after normalizing to a uniform film thickness, both aliphatic polyesters produce pure and embedded films with comparable water vapor permeabilities. Embedding urea or PCL-urea-IC crystals in both polyester films does not significantly affect their water vapor permeabilities. Dipping the pure and PCL-urea-IC embedded films in metha-
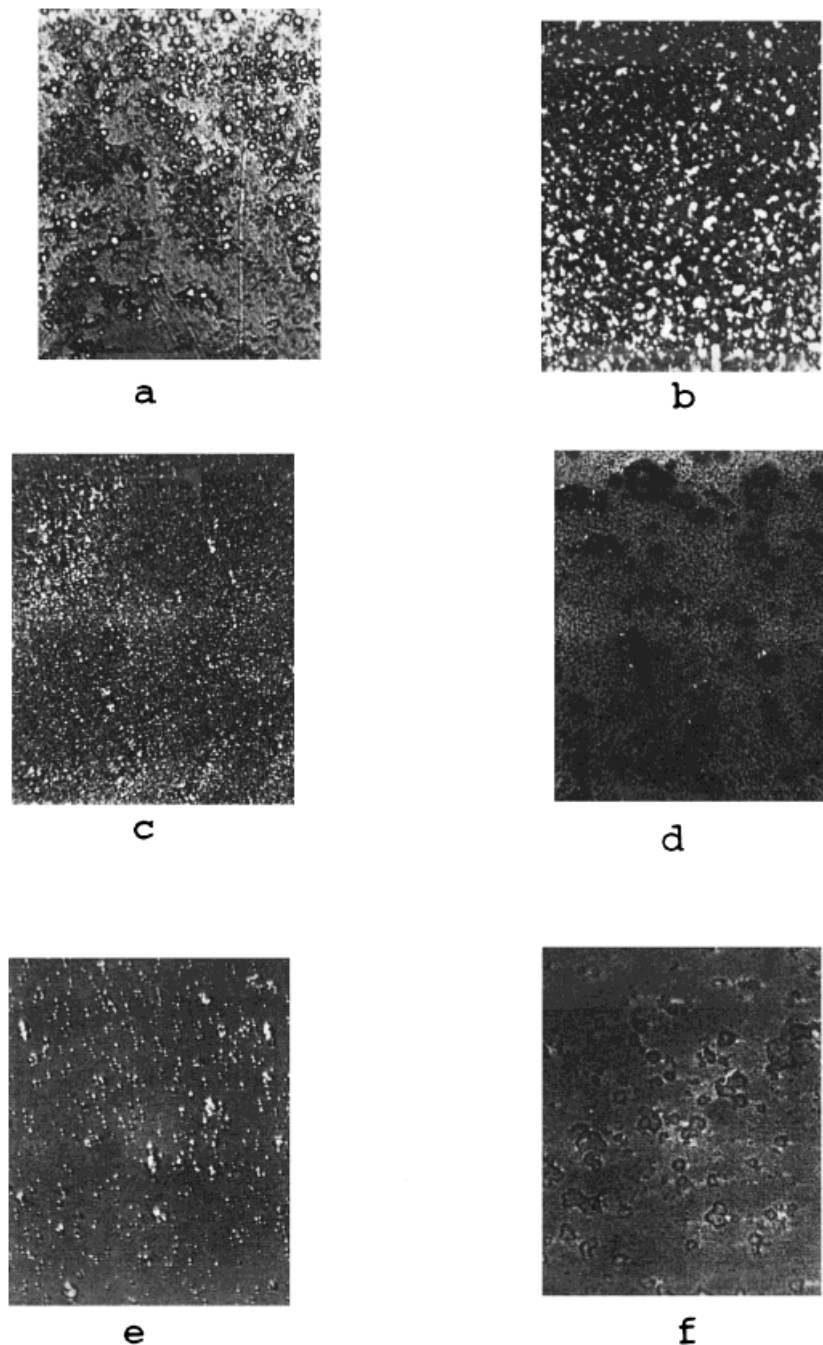
Figure 3 Low magnification (70×) micrographs of melt-pressed PCL (a, b), solution-cast PCL (c, d), and solution-cast PLLA (e, f) films embedded with PCL-urea-IC before and after dipping in methanol.

nol produces only modest increases in their observed water vapor permeabilities, while the permeability of water vapor through the urea-embedded films rises dramatically after the methanol dip, suggesting the formation of holes in the latter films which are sealed with PCL chains in the methanol-dipped, PCL-urea-IC embedded films. Even though no PCL endotherm is observed for

the PCL-urea-IC embedded and methanol-dipped PLLA film (Figure 5), the fact that this same film shows a water vapor permeability comparable to the undipped film suggests that PCL chains released from PCL-urea-IC crystals upon dipping have sealed the holes created by the dissolution of urea, but these same PCL chains are not crystalline. If no PCL chains remained in the metha-
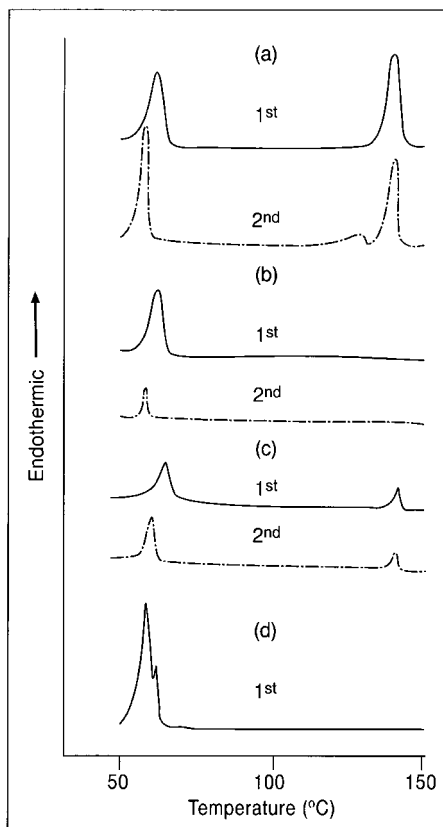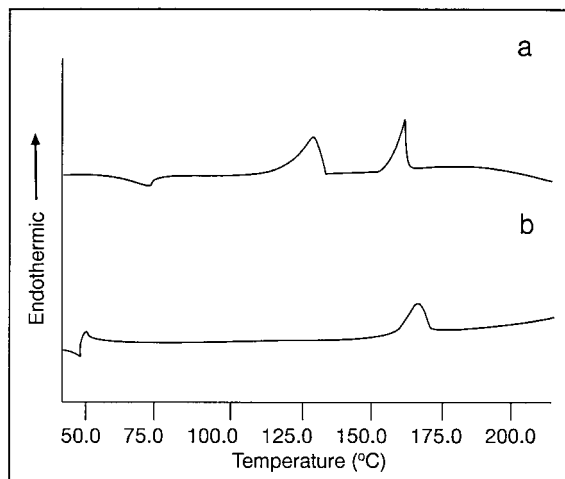
Figure 4 DSC scans of the solution-cast (a, b) and melt-pressed (c, d) films of PCL embedded with PCL-urea-IC before (a, c) and after (b, d) dipping in methanol.

nol-dipped PLLA film embedded with PCL-urea-IC, then we would expect a greatly enhanced permeability to water vapor of the dipped film compared with the undipped film, as was observed for the PLLA film embedded with urea before and after methanol dipping. We hope to employ FTIR and ^{13}C NMR observations of the undipped and dipped PLLA films embedded with PCL-U-IC to independently verify the presence of PCL chains in both samples.

It might be interesting to conduct careful annealing studies of these composite films and fibers in an attempt to control the types and amounts of crystalline morphologies developed. Of course we plan to study other physical properties of these samples, including their elongations, strengths, and moduli, while at the same time employing spectroscopic and diffraction techniques to more carefully define the organization of their constituent polymer chains.

We have demonstrated the ability to create polymer–polymer molecular composites by embedding polymer-urea-IC crystals into a carrier

Figure 5 DSC scans of the solution cast film of PLLA embedded with PCL-urea-IC before (a) and after (b) dipping in methanol.

polymer phase, followed by the subsequent release and coalescence of the IC-included polymer chains into the carrier polymer matrix. In this manner it should be possible to create a variety of phase-separated polymer composites with unique and controllable morphologies when the IC-included and matrix carrier polymers are chemically distinct. We would certainly expect phase-separated morphologies that are different from those obtainable by the traditional melt-blending and solution-casting techniques. By warming the polymer-IC fabricated composites to permit cen-
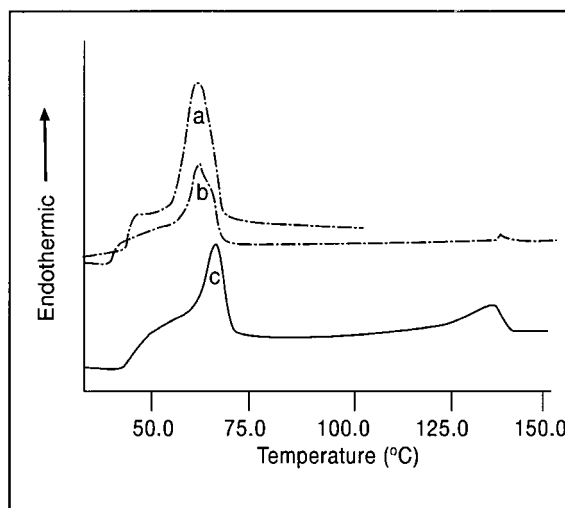
Figure 6 DSC scans of pure PCL fiber (a); PCL fiber spun with 2–3 wt% of embedded PCL-urea-IC (b); and PCL fiber spun with ca. 15–20 wt% of embedded PCL-urea-IC (c).

Table I Comparison of Thicknesses and Permeabilities of PCL, PCL-Urea, PCL-IC, PLLA, PLLA-Urea, and PLLA-IC Solution-Cast Films Before and After Dipping in Methanol

Sample Name	Average Thickness (mm)	Moisture Vapor Permeability (g/m^2/24 h)
PCL Film	0.022	375
Dipped PCL Film	0.010	440
PCL-Urea Film	0.139	413
Dipped PCL-Urea Film	0.313	747
PCL-IC Film	0.054	418
Dipped PCL-IC Film	0.076	583
PLLA Film	0.024	173
Dipped PLLA Film	0.041	187
PLLA-Urea Film	0.180	207
Dipped PLLA-Urea Film	0.155	540
PLLA-IC Film	0.045	183
Dipped PLLA-IC Film	0.052	236

ter-of-mass polymer chain diffusion, we expect to observe whether, and if so, how rapidly the IC-fabricated morphology is transformed into the morphology typical for melt-blended or solution-cast composites. Thus we may gain additional insight into both the equilibrium and kinetic aspects of phase separation in polymer blends.

Even if the IC-included and carrier matrix polymers are chemically identical, the sample resulting from the release and coalescence of IC-included polymer into the matrix will have two distinct populations of polymer chains, the predominantly chain-folded carrier polymer chains and the chain-extended, IC-coalesced chains. If both polymers are chemically identical save for the deuteration of one, then their temporal observation by neutron scattering, NMR, and other techniques should yield a measure of polymer self-diffusion from the morphology created by embedding and release of IC-contained polymer to the "equilibrium homogeneous" morphology, assuming deuteration does not seriously influence the molecular-level mixing of IC and carrier polymer chains. CPMAS/DD ^{13}C NMR observation of such a sample, where only the carrier polymer is deuterated, should evidence a time-dependent increase in signal intensity as the IC-released, protonated polymer begins to mix with the deuterated carrier polymer, thereby permitting the cross polarization (CP) of nuclear magnetization from the protons on the former to the deuterated car-

bons on the latter polymer, which when phase-separated would not otherwise experience CP nor be visible. Also, the number of deuterated carbons of the carrier polymer which are ultimately observed via CP from the protons on the IC-released polymer chains should provide us with a measure of the intimacy of mixing or the degree of entanglement between polymer chains in the equilibrated sample.

If deuteration were confined to the IC-embedded polymer, then the rate at which an extended polymer conformationally disorders to its plethora of flexible, randomly coiling conformations might also be estimated. The deuterated polymer chains coalesced from the urea-IC crystals into the protonated carrier polymer matrix should be in the extended-chain morphology. Once the sample temperature exceeds the melting point, both the deuterated, IC-derived and protonated, carrier polymer chains are free to diffuse and adopt their molten random coils. The temporal response of neutron scattering from the deuterated polymer chains should monitor their passage from extended conformations in phase-separated crystals into the equilibrium melt where they are random coils. Such observations might provide insights into the dynamic and equilibrium facets of crystallizing polymers from their melts, which are similar to, but the reverse of those from the above disordering and diffusion experiment. Similar observations made on samples composed of chemically distinct polymers, with deuteration of the carrier polymer, would monitor their mutual diffusion from the embedded morphology to the equilibrium, phase-separated morphology for that particular pair of polymers. Application of multidimensional solid-state NMR techniques can be utilized to monitor the same process and would eliminate the need for deuterated polymers.[20-26] The information generated in such experiments speaks directly to questions concerning both the dynamic and equilibrium aspects of phase separation in polymer blends.

In addition to the possible strengthening of fibers and films fabricated by embedding polymer-ICs into a carrier polymer phase followed by the release and coalescence of extended IC-derived polymer chains, several other applications can be envisioned for these polymer–polymer composites. Production of films containing islands of an IC-derived polymer in a sea of carrier polymer may result in a membrane whose permeability to gases and liquids differs among the phase-separated regions. If the IC-derived polymer islands are more permeable or may be removed from the

matrix carrier polymer of the film by dissolution, then membranes with porous regions or pores with controlled sizes may be fabricated.

It has been observed[27] that PCL and racemic poly(LD-lactic acid) (PLDLA) respond quite differently in biodegradation and drug-release studies. PLDLA films decompose at a rate three times that observed for PCL, while the release of steroids from PCL films is nearly two orders of magnitude faster than from PLDLA films. Clearly drug-release from polymer films is not directly tied to their overall macroscopic degradation. An optimal combination of both characteristics might be achieved by embedding PCL-urea-IC crystals in a PLDLA film, followed by the release and coalescence of the PCL chains from their U-IC crystals into the carrier PLDLA. In this manner a film composed of a readily degradable matrix (PLDLA) embedded with PCL domains, from which facile drug-release occurs, can be achieved. Such a composite film would serve as an effective drug-releasing implant, with the added benefit that the biologically inactive film portion of the implant (the drug container) would also rapidly degrade and be absorbed by the body. This suggested example is but one of many possible to visualize based on the unique phase-separated morphologies that are possible to create with polymers embedded, released, and coalesced from their IC crystals into a second polymer phase which serves as a carrier matrix.

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