Crystalline Memory on Polycarbonate

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Synopsis

A significant reduction on the time for thermal crystallization of Bisphenol-A polycarbonate
has been achieved by means of a previous crystallization step of the polymer in acetone, followed
by a capillary extrusion processing at temperatures above its melting range (230–280°C). The
crystallinity of PC was corroborated qualitatively by means of WAXS and quantitatively by
means of DSC. The acetone-crystallized polymer showed higher values of dynamic viscosity than
its amorphous counterpart. Such difference decreased with the increase of the test temperature
and disappeared at 280°C. The degree of crystallinity of thermally crystallized PC increased with
the decrease of the capillary extrusion temperature of the acetone-crystallized material. It is
inferred that the time–temperature-dependent long range molecular diffusion necessary for the
total melting of the crystal fractions could not take place entirely for the short times employed
($\approx$ 4 min), allowing the extruded polymer to behave as a self-nucleated material.

INTRODUCTION

Bisphenol-A polycarbonate (PC) is a linear polymer possessing a rigid
molecular backbone; for this reason, its thermal crystallization occurs at such
a slow rate that the material is well known as an amorphous polymer, when it
is processed under ordinary conditions.[1] If annealed at temperatures between
T_g and T_m, however, PC is able to crystallize though at a strikingly slow
rate.[1,2] Early studies[2] reported that annealing of very thin films (100 μm) took
8 days at 190°C for the first spherulites to appear. Another study[3] reported
the crystallization of 0.1 mm-thick films after annealing for 10 days at 190°C.
The first complete kinetic study of the crystallization of PC was published in
1964.[4] In that study, spherulitic growth rates were measured for very thin PC
films (50 μm), and the induction time for nucleation was reported as being
25 h.

From all the published data, it is evident that the PC crystallization is a
very slow process whose induction time is strongly dependent on the specimen
thickness. In a recent study,[5] 1-mm-thick PC specimens needed 76 days in
order to develop 12% crystallinity when thermally crystallized under vacuum
at 190°C.

Several attempts have been made to reduce the time for crystallization of
PC. However, such a goal has only been achieved through the incorporation of
either a plasticizer[1] or a solvent.[6] By means of the former, the crystallization

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rate is drastically increased; for instance, 2 days at 190°C are sufficient to fully crystallize (26%) a PC sample containing 8% DOP.[5] On the other hand, PC crystallizes at room temperature up to a 24% crystallinity in only 24 h, when immersed in acetone.[5] These two methods, however, have severe drawbacks: In the first case, the plasticizer cannot be easily removed; and in the second case, the solvent can only be extracted up to a certain extent, unless the sample is heated up to a temperature above T_g,[7] which causes strong changes in the solid sample. Furthermore, in both cases the crystallization takes place in the presence of an external agent.

The aim of the present work is to study the "crystalline memory" presented by PC, while developing a method to crystallize it isothermally in a rapid fashion. The idea is based upon the "crystalline memory" concept, which has been used to account for the melting behavior of polyethylene and polypropylene.[8-10] For those polymers it is well accepted that, when melted at temperatures just above their crystalline melting points ($T_m + 5°C$), a great number of crystalline nuclei still persist, allowing the polymers to crystallize faster upon cooling, due to the skipping of the induction time for nucleation. Their crystallization, hence, takes place as for heterogeneous (self-nucleated) systems.[10]

The "crystalline memory" effect vanishes when the polymer is either kept at the melting temperature for a long time, or heated, well above its melting point. When one of such conditions is met, the nuclei melt and the polymer crystallizes at its normal rate.[8-10]

In this work, the quick crystallization by acetone immersion is taken as a vehicle to create crystal nuclei which, if kept after solvent extraction and further melting, will significantly shorten the time for the overall crystallization and will allow the study of their effect on thermal crystallization of PC from the amorphous state.

EXPERIMENTAL

Materials

The material used in the present work was extrusion-grade Bisphenol-A polycarbonate, manufactured by Bayer (Makrolon 3203). $M_v = 31.500$ g/mol.

Technical-grade acetone was used to precrystallize the polymer. The solvent employed for the solution viscosity measurements was analytical-grade THF, supplied by Merck.

Acetone Crystallization

The PC pellets were crystallized by acetone immersion at room temperature. Such immersion caused a rapid whitening, which has been related to crystallization. The immersion was sustained for 24 h, to ensure the maximum degree of crystallinity.[11]

After immersion, the acetone was decanted and the pellets ˙   ˑredried in a forced convection oven at 30°C for 24 h. Subsequently, the p   were dried in a nitrogen-purged vacuum oven at 26 psi and 165°C for 48 n.

Gravimetric determinations of the residual acetone content after drying showed that this was lower than 0.5% of the sample weight.
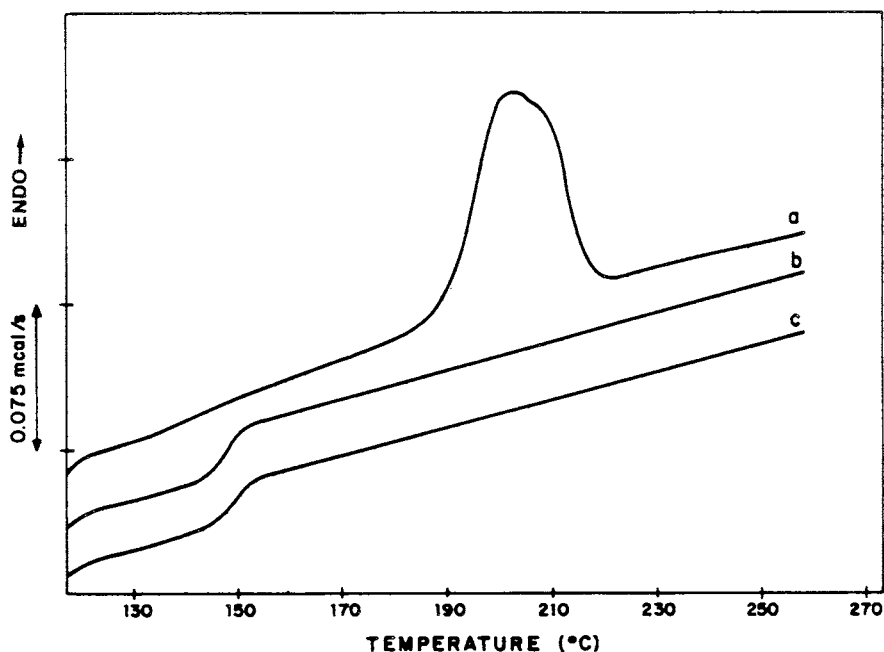
Fig. 1.   DSC thermograms corresponding to: (a) acetone-crystallized sample; (b) amorphous pellets; (c) acetone-crystallized after capillary extrusion at 230°C.
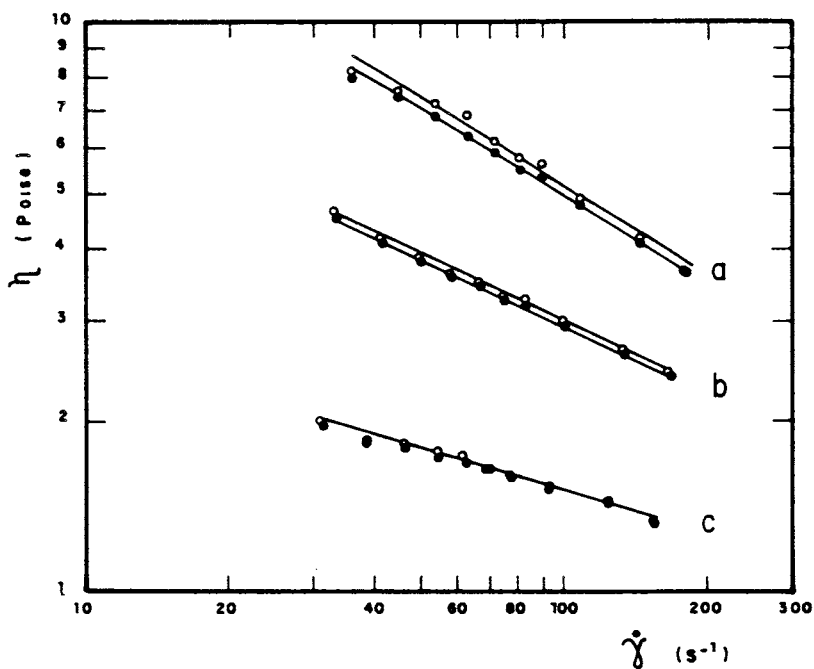

Fig. 2.   Dynamic viscosity vs. shear rate plots for acetone-crystallized (○) and amorphous (●) PC, taken at: (a) 230°C; (b) 250°C; (c) 280°C.

Rheological Measurements

A Gottfert Rheograph 2000 capillary rheometer, with a 20/2 length/diameter ratio was used for the dynamic viscosity determinations. Such rheometer acted also as a small scale extruder, in which all the acetone-crystallized samples were thermally processed. The measurements were performed isothermally at temperatures of 230, 240, 250, 260, 270, and 280°C. The same procedure was applied to the amorphous (virgin) samples. The polymer amount used in all measurements was 8 g; this amount allowed the minimization of the melting-compactation time, prior to extrusion, down to 4 min.

Wide Angle X-Ray Scattering (WAXS)

WAXS studies were conducted in a Phillips 1730 X-ray generator, using $CuK\alpha$ radiation (Ni filter) and equipped with a Warhus vacuum flat plate camera.

Differential Scanning Calorimetry (DSC)

DSC tests were performed with a computer-equipped Perkin-Elmer DSC-2C instrument. The temperature range studied was 117–262°C, with a sensitivity
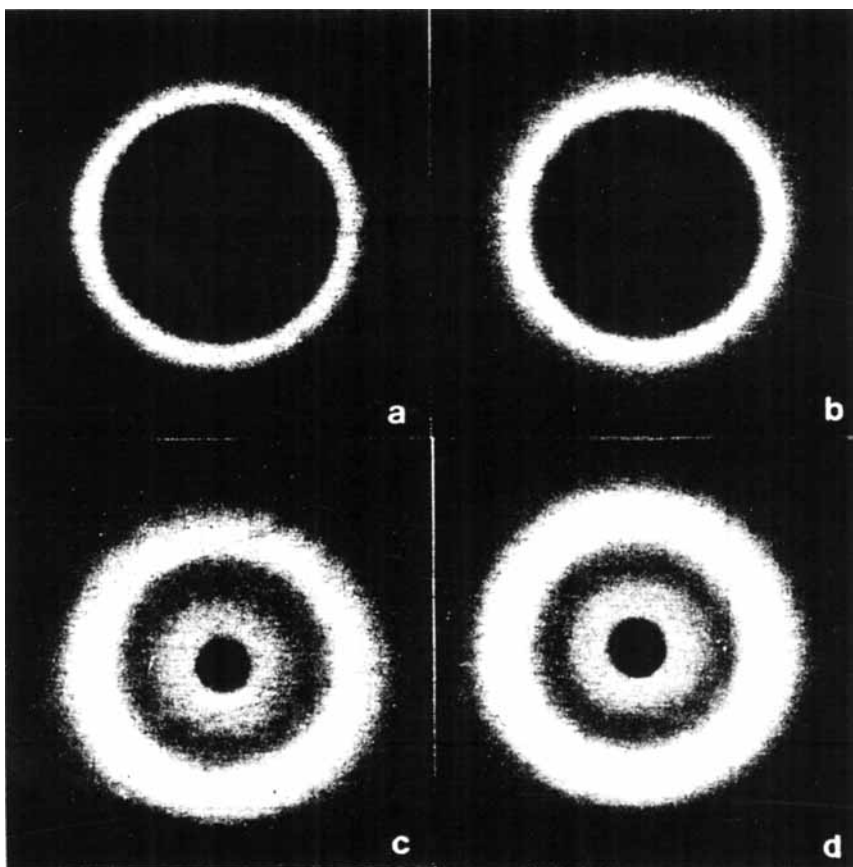

Fig. 3.   Diffraction patterns corresponding to: (a) amorphous/230°C capillary extruded PC, after 156 h annealing at 190°C; (b) acetone-crystallized/230°C capillary extruded PC, after same annealing process; (c) amorphous/230°C capillary extruded PC without annealing; (d) acetone-crystallized/230°C capillary extruded PC without annealing.

of 0.3 mcal/s (full scale) under nitrogen atmosphere and with a 20°C/min scanning rate. All thermograms were weight-normalized prior to plotting. The percents of crystallinity were calculated through the DSC-determined ΔH_m, taking the ΔH_m^0 of the pure crystal as 26 cal/g.[6]

RESULTS AND DISCUSSION

The acetone-immersed pellets were completely white in appearance after the extraction of the acetone, and the polymer did not show any difference on M_v after the immersion. The white appearance is due to crystallization, and it was demonstrated by the melting endotherm observed on its DSC thermogram [Fig. 1(a)]. Such endotherm ranged from 191 to 218°C, and its corresponding degree of crystallinity was 19%. The thermogram of the amorphous pellets is shown in Figure 1(b).

The results of the dynamic viscosity (η vs. $\dot{\gamma}$) determinations at three of the testing temperatures 230, 250, and 280°C are shown in Figures 2(a), 2(b), and 2(c), respectively, for the acetone-crystallized PC (○), together with the corresponding results for the amorphous polymer (●). It can be observed in Figure 2 that the dynamic viscosity values belonging to the acetone-crystallized polymer were always higher than the values corresponding to the amorphous one, and their difference diminished gradually with the increase of
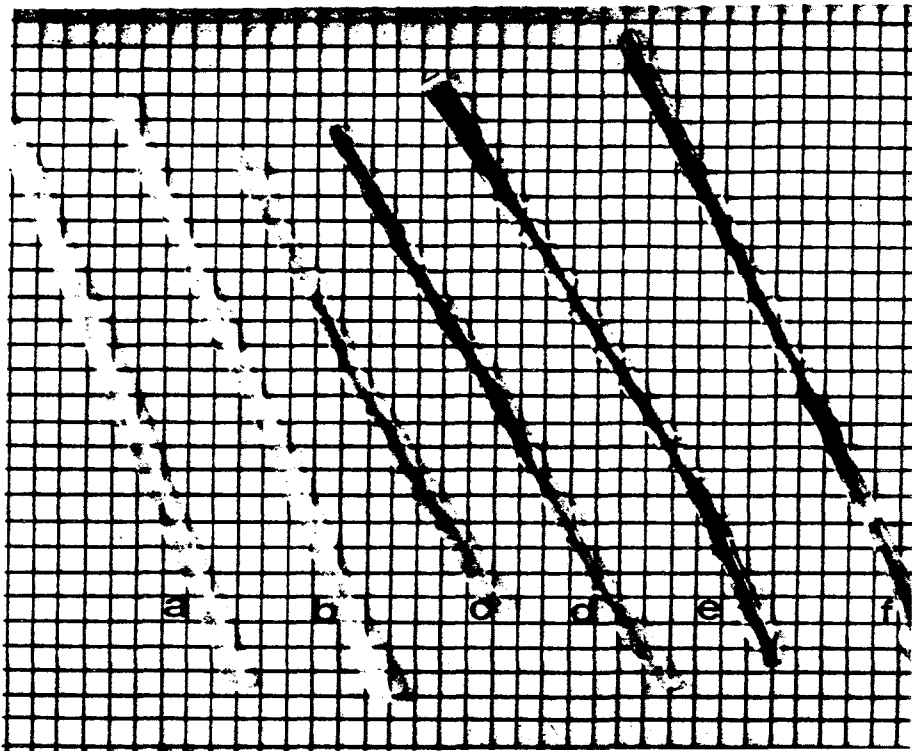

Fig. 4. Optical appearance of the amorphous/capillary extruded PC, after 156 h annealing at 190°C. Extrusion temperatures: (a) 230°C; (b) 240°C; (c) 250°C; (d) 260°C; (e) 270°C; (f) 280°C.

the processing temperature. This was observed at all the temperatures studied. At 280°C, the difference in viscosity became null and the η vs. $\dot{\gamma}$ curves equaled for both polymers.

The results mentioned above may well be attributed to the effect of residual short range order (or crystalline content), which persists during the thermal processing of the acetone-crystallized samples, increasing their dynamic viscosity, in comparison with the amorphous samples. The gradual approaching of the rheological curves with increasing process temperature may well be attributed to a gradual decrease of such short range order, which disappears totally at 280°C, i.e., the "crystalline memory" is erased. Persistence of some extents of order at temperatures around the melting range has been studied for other polymers,[8-10] and, in light of the present results, it may occur in PC even at temperatures well above its melting range. It is worth noticing that the differences in the rheological curves just described only apply for the processing times employed (~ 4 min) as, for longer times, the same trend would be expected, although shifted toward lower temperatures.

All samples (amorphous and acetone-crystallized PC) were completely transparent in appearance after being extruded through the capillary rheometer, indicating their amorphous nature. This was confirmed by DSC and WAXS. as shown in Figures 1(c) and 3(d), respectively (for the acetone-crystallized/230°C capillary extruded sample) and in Figure 3(c) for the amorphous 230°C capillary extruded one, whose DSC thermogram (not shown) was similar to Figures 1(b) and (c). The amorphous nature is evident in the
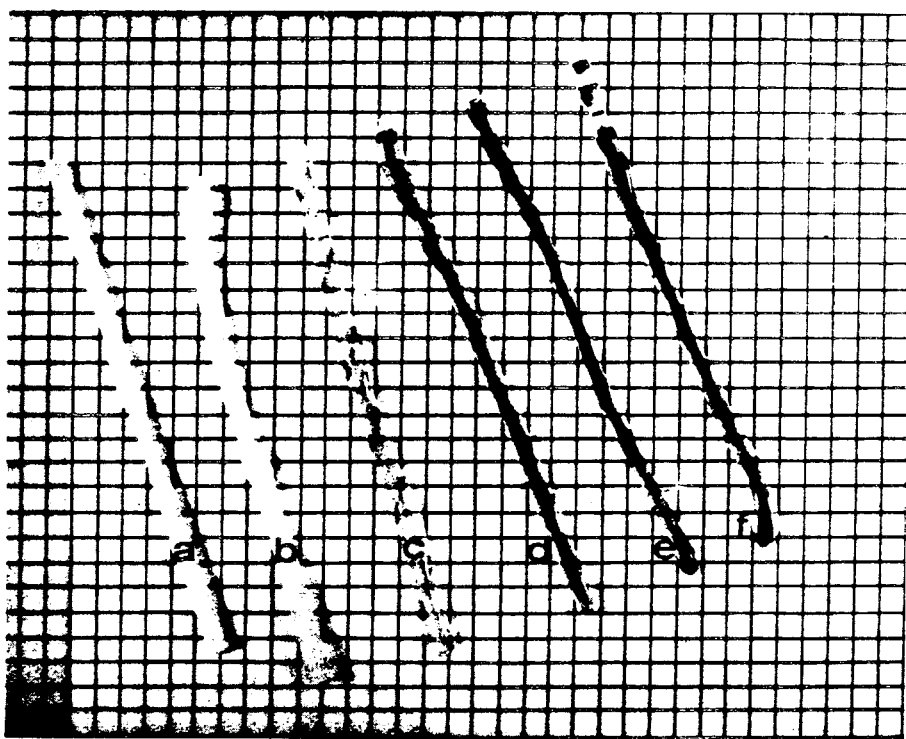

Fig. 5.   Optical appearance of the acetone-crystallized/capillary extruded PC samples, after 156 h annealing at 190°C. Extrusion temperatures: (a) 230°C; (b) 240°C; (c) 250°C; (d) 260°C; (e) 270°C; (f) 280°C.
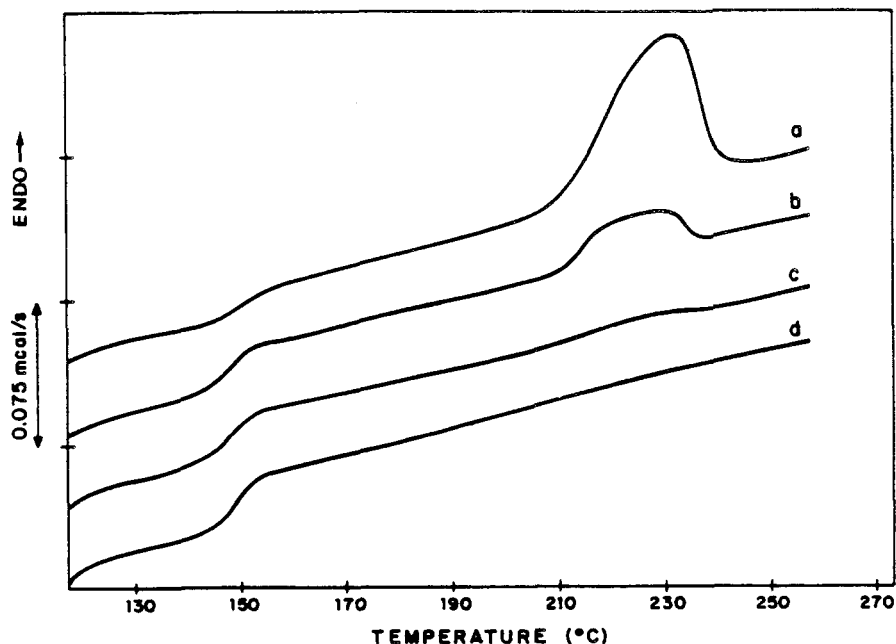
Fig. 6.   DSC thermograms of the acetone-crystallized/capillary extruded PC samples, after 156 h annealing at 190°C: (a) extruded at 230°C; (b) extruded at 240°C; (c) extruded at 250°C; (d) amorphous/230°C extruded, followed by annealing at 190°C for 156 h.

thermogram due to the lack of a melting endotherm and in the diffraction patterns, by the presence of only an amorphous halo. The transparent samples were then subjected to annealing at 190°C under vacuum, in order to follow the development of crystallinity. Figures 4 and 5 show the optical appearance of samples after 156 h annealing at 190°C; in Figure 4 are seen the amorphous-PC samples extruded at temperatures from 230 to 280°C, showing an appearance ranging from translucent (i.e., 230 and 240°C), to clear as the extrusion temperature was increased (i.e., 260 to 280°C). In Figure 5 are seen the acetone-crystallized samples after being treated under the same extrusion and annealing conditions as samples of Figure 4. Their optical appearance however, goes from opaque (i.e., 230 and 240°C) to translucent (i.e., 250 and 260°C) to clear (i.e., 270 and 280°C).

All changes in sample transparency can be taken as changes in crystallinity, the more opaque the sample, the higher the crystallinity developed under the annealing process. This was confirmed by the following results: Figures 6(a)–6(c) show how the area of the endotherm of melting decreases on going from the 230°C extruded acetone-crystallized sample to the one extruded at 250°C. Calculations based on such thermograms are presented in Table I. On the other hand, Figure 6(d) shows the thermogram of a 230°C extruded amorphous PC, which barely developed some DSC-detectable crystallinity [being its thermogram very similar to the one shown in Fig. 1(c)], although subjected to the same extrusion and annealing treatments than the acetone-crystallized PC sample of Figure 6(a). Figures 4(a) and 5(a) show the variation in optical appearance of samples corresponding to thermograms presented in Figures 6(d) and 6(a), respectively. It can be observed that the acetone-crystallized PC sample is completely opaque while the amorphous PC

TABLE I
Calculations Based on DSC Thermograms of Figures 1 and 3

Processing temperature (°C)	T_m onset (°C)	ΔH_m (cal/g)	Crystallinity (%)
NP[a]	190	5.03	19
230	210	3.63	14
240	211	1.21	5
250	213	0.26	1

[a] NP = nonprocessed.

sample is only translucent. This translucency is due to a low degree of crystallinity, barely detected by DSC, but observable by WAXS, as shown in Figure 3(a), where the photograph was overexposed during printing, in order to enhance the evidence of the thin white ring 17.1° (2θ) denoting incipient crystallinity, which otherwise would be covered by the strong amorphous halo. A well-developed crystallinity is shown instead in Figure 3(b) for the acetone-crystallized PC sample processed at 230°C and annealed at 190°C during 156 h.

CONCLUSIONS

Capillary extrusion at temperatures above the melting range of acetone-crystallized PC can leave either some extent of molecular order or small crystalline fractions, which are undetectable either by DSC or by WAXS. Such crystalline residua can strongly reduce the time for thermal crystallization during annealing, probably by skipping the nucleation step (induction time), causing PC to behave as a self-nucleated polymer.

The acetone-crystallized PC shows higher values of dynamic viscosity than the amorphous polymer at all temperatures. The differences between the η vs. $\dot{\gamma}$ curves decrease gradually with the processing temperatures, becoming null at 280°C, temperature at which the processing times used, helped to erase all the "crystalline memory" left by the acetone crystallization.

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