Colloidal Macromolecular Phenomena.
Part II.   Novel Microcrystals of Polymers

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Synopsis

Colloidal microcrystalline cellulose, introduced in 1961, now is a successful commercial product with growing world-wide markets. This paper describes some major findings of our continuing research to convert fibrous or fiber-forming polymer systems into new colloidal microcrystalline physical states without going through a homogeneous molecular solution phase. Several novel microcrystalline colloidal products from the following natural and/or synthetic polymeric raw materials are described and compared for the first time: cellulose, amylose, collagen, nylon, and chrysotile mineral silicates. Many previously unpublished electron micrographs are presented. These products demonstrate a new and growing field of colloidal microcrystalline polymer science. They open up increasing opportunities for new polymer products based on the original concept, namely, the unhinging of polymer microcrystals from their natural or synthetic network and then by appropriate mechanical energy, releasing them as discrete, submicron colloidal polymer microcrystals dispersed in various liquid media to form unique gel systems, or reaggregated in the dry state to form porous colloidal particles.

Colloidal microcrystalline celluloses as new, stable, thixotropic gel systems involving aqueous colloidal dispersions of disintegrated level-off D.P. cellulose, abbreviated as $\overline{D.P.}$,[1,2] at high solids concentration were first described in a patent issued in 1961.[3] This patent, along with a later publication,[4] described a combination of two specific prerequisites for producing novel colloidal phenomena from a fibrous high polymer such as cellulose: (*1*) a controlled chemical pretreatment to destroy the molecular bonds whereby microcrystals are hinged together in a network structure, and (*2*) appropriate use of mechanical energy to disperse a sufficient amount of the unhinged microcrystals in the aqueous phase to produce the characteristic novel rheology and the smooth, fatlike spreadability of the resulting colloidal microcrystalline cellulose gels. It was clearly demonstrated that stable gel systems were obtained only when the mechanical energy was introduced into an aqueous suspension of level-off D.P. cellulose in which the total solids concentration was of the order of

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* This term originally defined for cellulose,[1] refers to the weight-average molecular weight (expressed as degree of polymerization) of the macromolecules comprising the discrete, colloidal, unhinged microcrystals of polymers.

5% or more, and only if the mechanical energy was severe enough to liberate a minimum number of microcrystals to make a stable gel possible.

Unlike many gel systems based on molecular dispersions of macromolecules, colloidal microcrystalline cellulose gels possessed unusually stable viscosities. Even on prolonged standing, the viscosity values of these structural gels remained constant; in other words, microcrystalline cellulose gels never became rubbery with time as is so characteristic of gels based on the dispersions of hydrophilic macromolecules, such as the various natural and synthetic gums.

More recently,[5,6] a detailed comparison of two microcrystalline gel systems was made. Commercial microcrystalline cellulose (Avicel, FMC Corporation), comprising rodlike, submicron, and discrete microcrystals extracted from a natural fibrous polymer (cellulose), was compared with microcrystals of colloidal alumina (Baymal, E. I. du Pont de Nemours & Co., Inc.) grown synthetically from a solution of a basic aluminum salt. Electron microscopy reveals clearly that the size and shape of the respective microcrystalline particles were remarkably similar. An even more striking fact, however, is that, despite the great disparity in chemical composition, colloidal dispersions, creams, and gels of these materials possess very similar rheological, physical, and functional properties. This is the nexus of the novelty and of the practical importance of reducing well-defined molecular aggregations of high polymeric materials to truly colloidal dimensions, namely, circular or rectangular rods or platelets of the order of 25–300 A. wide × 25–300 A. thick × 50–5000 A. long. We believe that these phenomena represent a novel segment of polymer chemistry. They are associated with the unique physical behavior of discrete, colloidal, and ordered aggregates of many long chain molecules. The dimensions of these particles lie roughly between those of the smallest viruses and small bacteria.

The above-noted two microcrystalline systems were predicted[5,6] to be forerunners of other colloidal microcrystalline macromolecular products. New systems might also be fashioned by means of a similar mechanism—namely, a chemical or other type of pretreatment to sever or eliminate the interconnecting regions of low lateral order consisting of molecular chains weaving in and out of the microcrystals, followed by effective mechanical disintegration to dislodge them from their natural architectural positions. It was envisioned that a host of novel products could be fashioned from both synthetic and natural high polymers, from organic as well as inorganic high polymers, or combinations of both of them.

This paper is a report of some major findings of our continuing research in this field. It provides comparative results for microcrystalline products made from the following polymeric materials: cellulose, amylose, collagen, nylon, and chrysotile mineral silicates. Colloidal alumina comprising similar microcrystals, prepared by controlled "synthesis" from solution, is discussed in relation to the foregoing examples.[7]

Microcrystalline Cellulose

The size and shape of microcrystals recoverable in the form of stable colloidal dispersions of cellulose are largely determined by the nature of
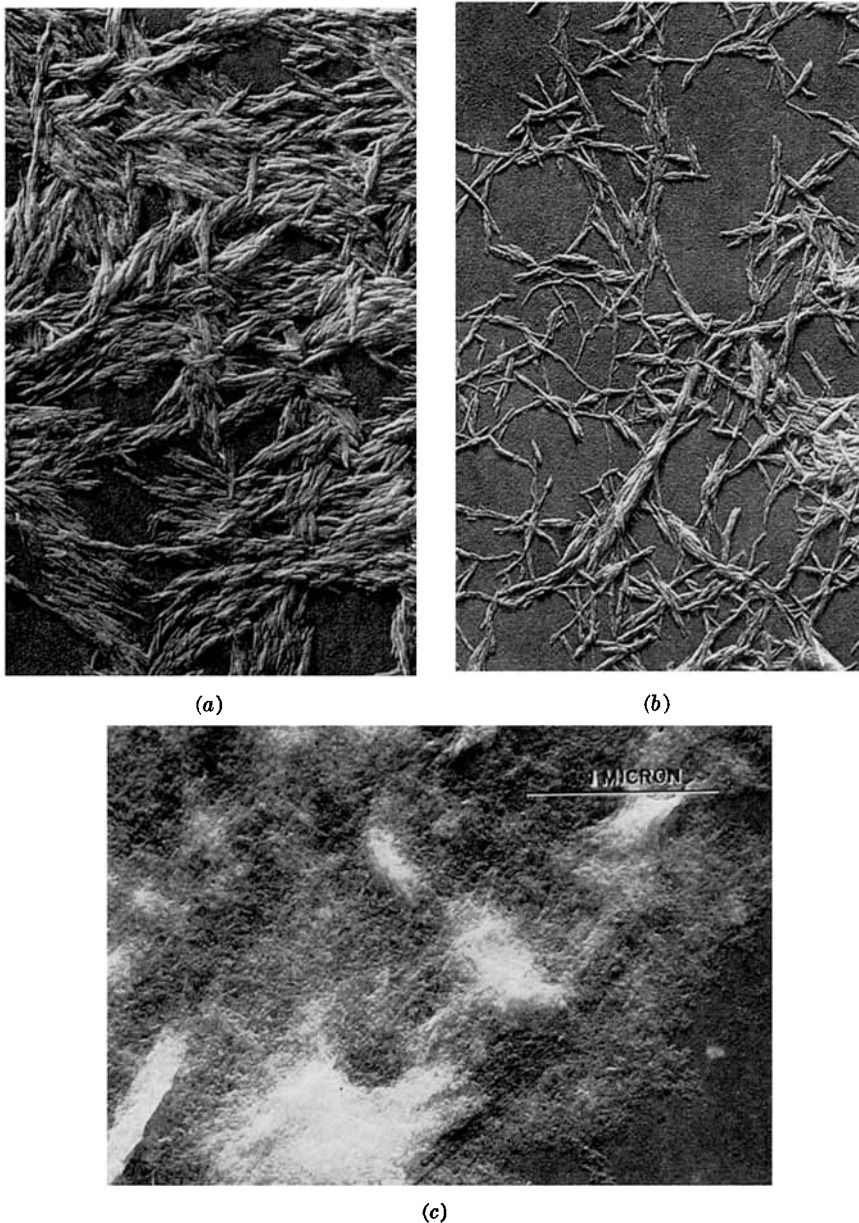

(a)   (b)

(c)

Fig. 1. Microcrystals of (a) cotton cellulose, (b) wood cellulose, and (c) cellulose recovered from rayon tire cord.   25,000×.

the starting raw material, especially by whether the cellulose is in its native or regenerated state.[1,2] For example, a representative spectrum of such microcrystals is illustrated by Figure 1, which shows microcrystals of cotton linters, microcrystals of wood pulp, and rayon (regenerated cel-
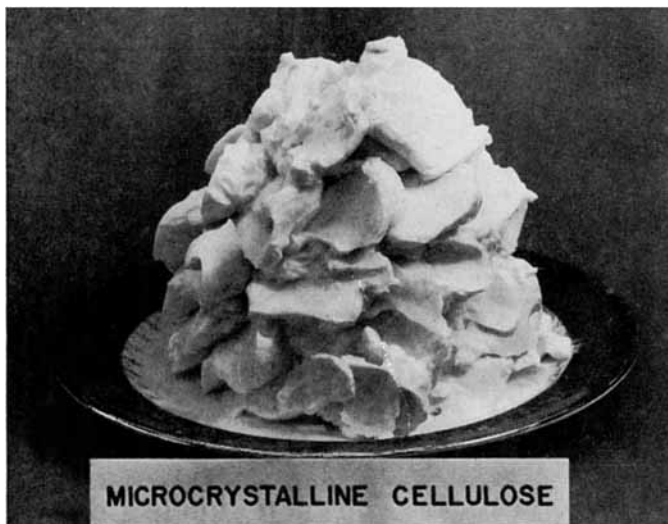
Fig. 2. Aqueous microcrystalline cellulose gel, 14% solids.

Fig. 3. Microfibrils of beaten wood pulp.   7,500×.

lulose).   The average length of each type of microcrystal corresponds approximately with the measured level-off D.P. of each sample.   It is especially pertinent to compare Figures 1b and 1c.   The level-off D.P. of wood cellulose microcrystals is 220, whereas the level-off D.P. of the cellulose in rayon tire cord microcrystals is only about 20.   These electron micrographs clearly illustrate this tenfold difference in microcrystal lengths.   Of further interest is the fact that the microcrystals recovered from a melt-regenerated synthetic polymer (nylon) are almost identical with the regenerated cellulose tire cord rayon microcrystals (compare Figs. 1c and 12).

Stable microcrystalline cellulose gels and dispersions may be made from all three types of level-off D.P. cellulose.[3]   A sample of a 14% gel made from level-off D.P. wood pulp cellulose is shown in Figure 2. An electron micrograph of beaten wood pulp fibrils in which the microcrystals are still hinged together by primary molecular bonds is shown in Figure 3.   This is the raw material from which the gel in Figure 2 was made, after conversion to its level-off D.P.

Microcrystalline Amylose

A commercially available form of amylose, Nepol (A. E. Staley Mfg. Co.), was used as the raw material to produce stable microcrystalline amylose gels and dispersions.

An electron micrograph of the starting material is shown in Figure 4. This raw material contained amylose fibrils as well as evidence of a significant amount of flat lamellae.   It is not known whether the flat lamellae were present in the initial starch stock from which the amylose product was isolated by fractionation, or whether these lamellar particles arose as a result of the fractionation procedures used to concentrate the amylose from the amylopectin.

Subjection of amylose of Figure 4 to a careful chemical pretreatment (acid hydrolysis) followed by washing and subsequent mechanical dis-
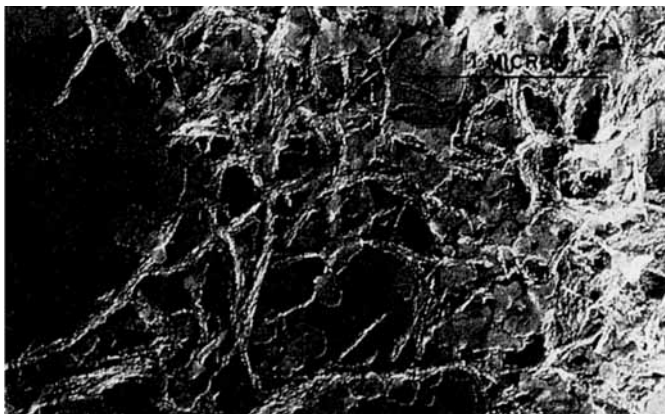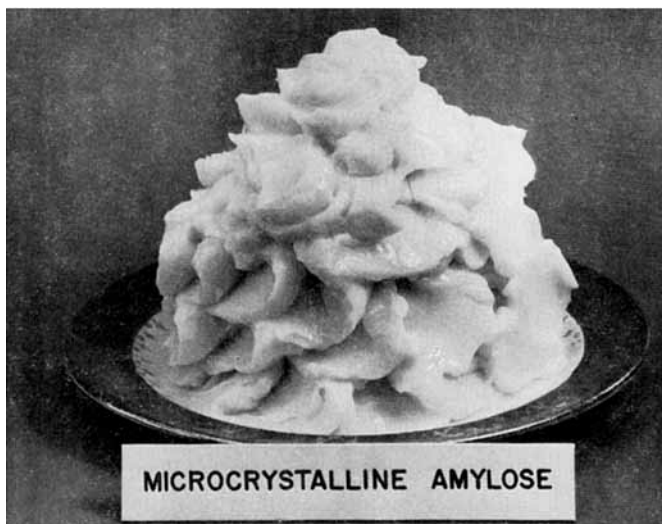

Fig. 4. Commercial amylose starch.   25,000×.

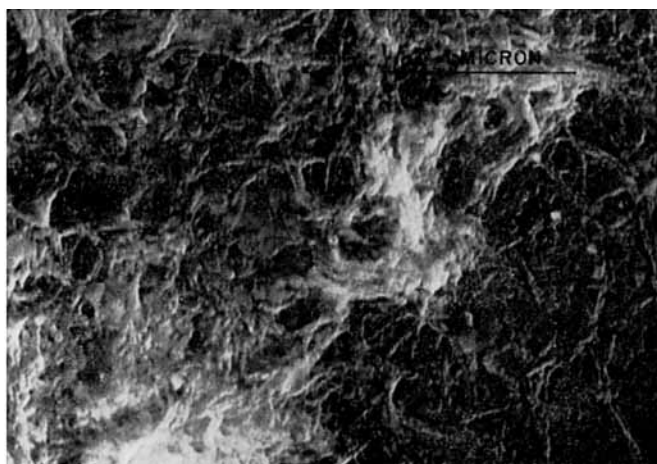Fig. 5. Aqueous microcrystalline amylose gel, 12%.

Fig. 6. Microcrystals of amylose from Nepol starch.   25,000×.

integration at 12% solids in a Waring Blendor for 15 min. leads to an un-
usually stable amylose gel (Fig. 5).   An electron micrograph of the micro-
crystals in the amylose gel (acid-insoluble fraction) showing the striking
beaded structure of the individual amylose microcrystals, is given in Fig-
ure 6.   Only flat crystalline lamellae, however, were recovered from the
acid-soluble fraction obtained after the completion of the hydrolytic pre-
treatment.   An excellent electron micrograph (Fig. 7) was obtained upon
drying down a droplet of acid soluble fraction showing the flat crystalline
lamellae.

In Figure 8, the x-ray diffraction diagram of the commercial Nepol
amylose raw material (Fig. 4) is compared with the x-ray diffraction
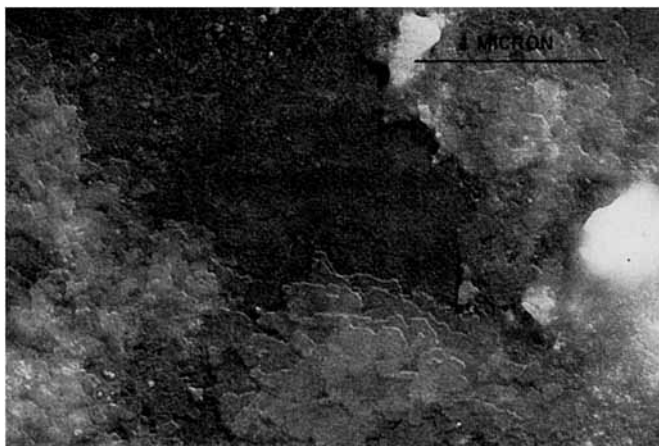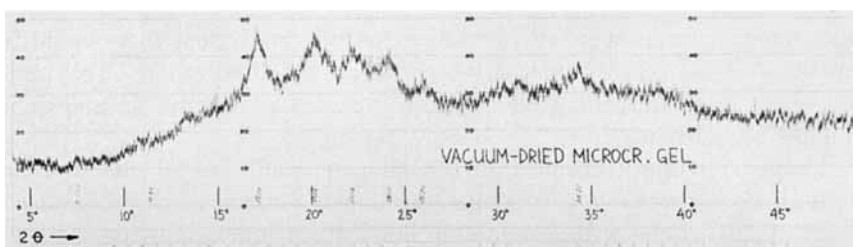
Fig. 7. Crystalline lamellae from acid-soluble fraction of amylose digestion. 25,000×.
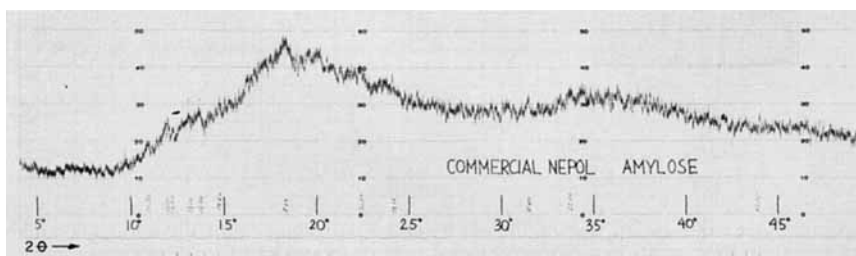
(a)

(b)

Fig. 8. X-ray diffraction tracings for (a) amylose and (b) microcrystalline amylose. CuKα radiation.

diagram of the fraction of amylose microcrystals (Fig. 6).   The increased crystallinity of the recovered amylose microcrystals is clearly evident.

Microcrystalline Collagen

Bovine hide collagen is a natural fibrous polymer of high molecular weight.   It exhibits a lower lateral order (less crystalline) than cellulose or amylose, but does give a definitive x-ray diffraction pattern (Fig. 9a). The chemical pretreatment, accordingly, for conversion of the collagen
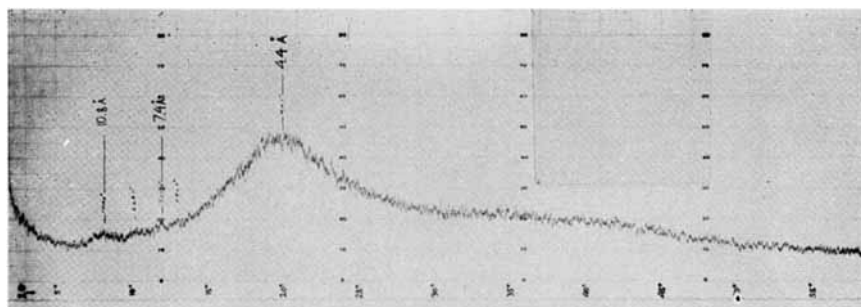
(a)
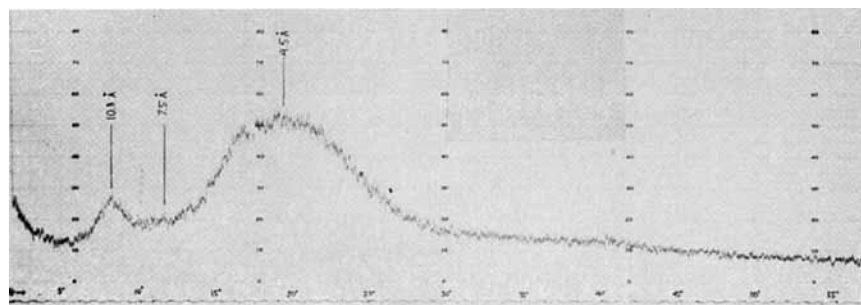
(b)

Fig. 9. X-ray diffraction tracing for (a) bovine hide collagen and (b) a form of micro-
crystalline collagen.   CuKα radiation.

to a microcrystalline particulate state is quite critical, and the mechanical
disintegration step must also be more carefully controlled than would be
the case with a polymer having a high degree of lateral order.   This proc-
ess leads to a sharpening of the x-ray diffraction pattern as shown in
Figure 9b, particularly in the 10.8 A. region.

Under carefully controlled and combined conditions of pH and at-
trition, viscosity-stable gels comprising largely submicron discrete micro-
crystalline particles with a minimum build up of individual tropocollagen
molecules can be prepared.

Rodlike microcrystalline particles comprising bundles of tropocollagen
molecules with maximum dimensions well under 1 μ are shown in Figure
10a.   Spherical, discrete microcrystalline particles of bovine hide col-
lagen, prepared by filtering an aqueous dispersion consisting of particles
shaped as in Figure 10a through a sintered glass filter, are shown in Figure
10b.   Note especially that a distribution of discrete particles ranging in
size from a small virus (25 A.) to that of a small bacterium (5000 A.)
is obtained by filtering the more rodlike particles of microcrystalline col-
loidal collagen through the fine pores and channels of a sintered glass
filter.   Figure 11 shows a viscosity-stable aqueous gel of microcrystalline
colloidal collagen at only 1.0% solids.   The viscosity stability of these
gels is unique; unlike aqueous solutions of gelatin or acidic solutions of

(a)
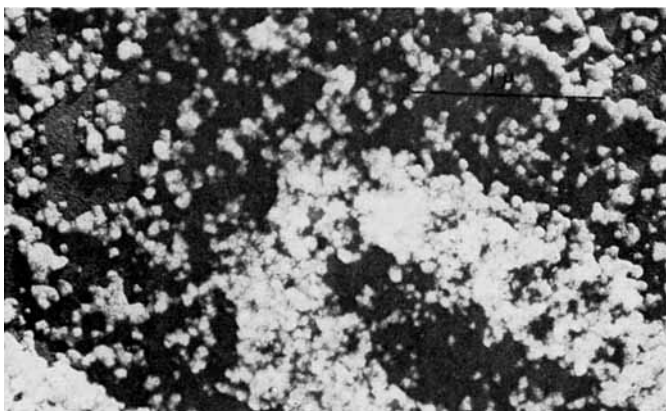
(b)

Fig. 10. Microcrystals of bovine hide collagen: (a) microcrystals;   (b) spheroidized microcrystals.   25,000×.

individual tropocollagen molecules, the viscosity of microcrystalline collagen gels remains constant with time of standing at 25°C.

Microcrystalline Polyamides

The possibility of unhinging and liberating microcrystals from a fiber-forming synthetic organic polymer was also investigated.

Paper-grade nylon fibers were given an appropriate acid hydrolysis treatment which precluded solution of the fibers and caused a limited amount of swelling at the surfaces of the microcrystals.   Figure 12 is an electron micrograph of single nylon microcrystals.   It is particularly noteworthy to observe the similarity in size and shape of these microcrystals with those obtained from regenerated cellulose (see Fig. 1c).   Once again, characteristic, smooth, stable and easily spreadable aqueous gels were prepared from nylon microcrystals (Fig. 13).
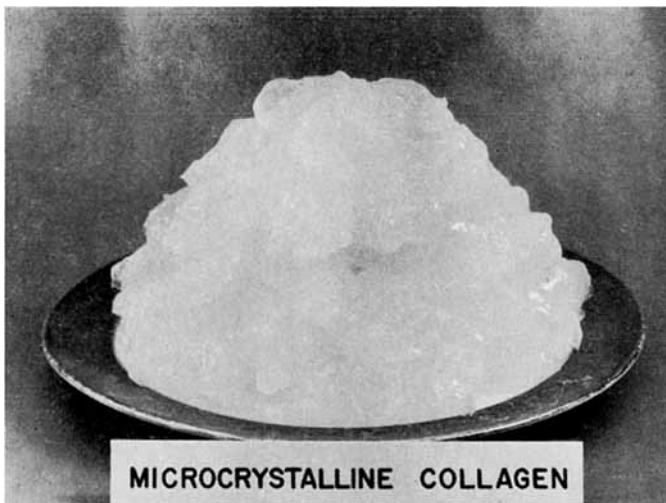
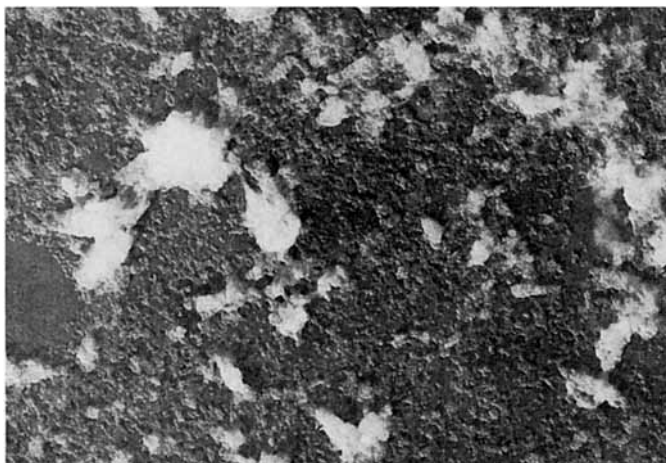Fig. 11. Aqueous microcrystalline collagen gel, 1% solids.

Fig. 12. Unhinged microcrystals of nylon.   25,000×.

Microcrystalline Silicates

Chrysotile asbestos is an abundant, fibrous, natural inorganic polymer. It consists of very long fibrils, now believed to contain hollow cores,[8] and Figure 14 shows individual chrysotile fibrils.   The goal in this instance was to pretreat the chrysotile fibrils in such a manner that they would be receptive to mechanical disintegration which would convert the very long natural fibrils into microcrystalline rodlike particles under 5000 A. in length.   Prior evidence[4-6] led to the hypothesis that if fibrous silicate polymers could be reduced to colloidal particles under $1/2$ μ in maximum dimension without involving solution and precipitation, novel stable gel products should result.

Upon subjecting chrysotile fibers to an appropriate acid pretreatment followed by relatively severe mechanical disintegration, it was discovered that microcrystals having dimensions of the same general order of magnitude as cellulose microcrystals could be liberated, and the resulting product possessed striking gelling properties, especially in moderately polar media.
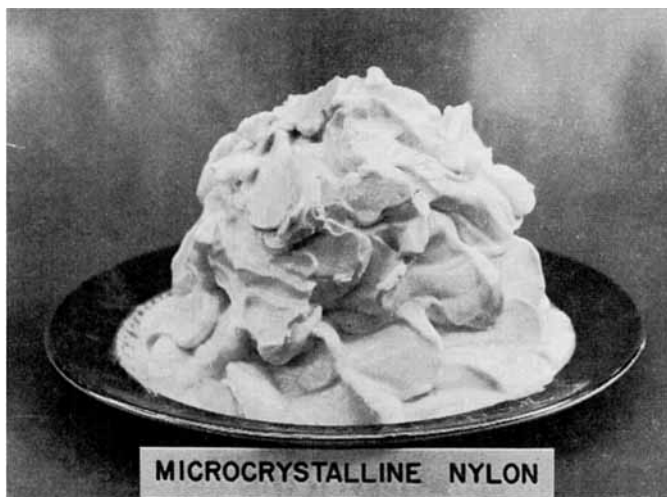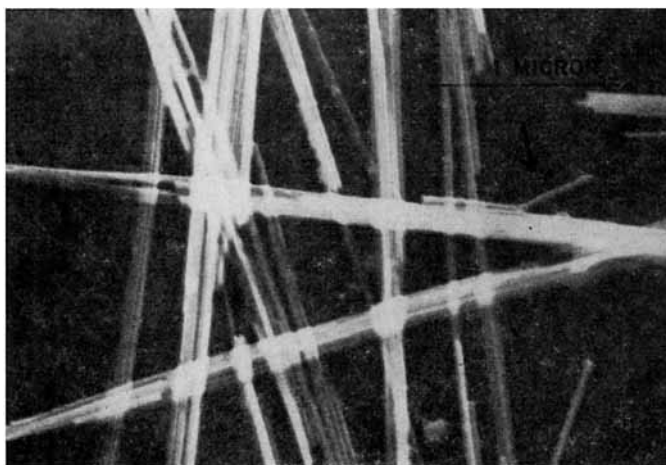

MICROCRYSTALLINE   NYLON

Fig. 13. Aqueous microcrystalline nylon gel, 22%.

Fig. 14. Single fibrils of dispersed chrysotile asbestos.   12,500✕.

Figure 15a is an electron micrograph showing the microcrystals of the chemically pretreated and mechanically disintegrated chrysotile.   Once again, the microcrystals possess rod-like structures and are submicron. Figure 15b is a particularly valuable electron micrograph, in that it

(a)

(b)

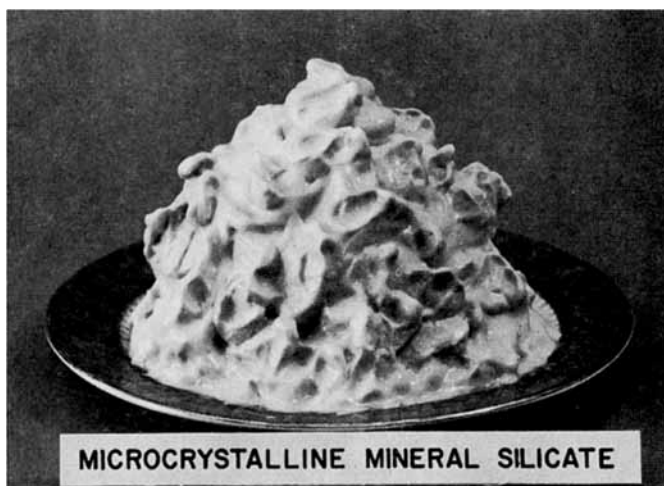Fig. 15. Microcrystalline mineral silicate: (a) microcrystalline particles; (b) microcrystal formation.   25,000✕.

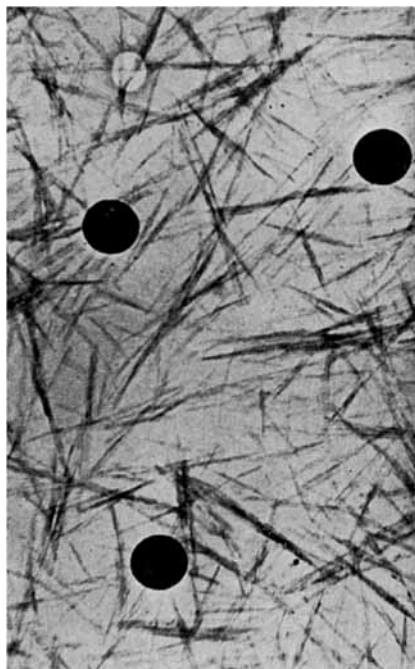Fig. 16. Aqueous microcrystalline mineral silicate gel, 8%.

Fig. 17. Microcrystals of colloidal alumina.   25,000×.

shows a single rodlike microcrystalline silicate particle with dimensions approximately 200 × 4000 A. breaking off from a long microfibril.

Such microcrystalline silicate particles when dispersed, for example, in water, glycerin or glycols, tricresyl phosphate, or silicone oils, serve as most effective thickening agents leading to gels similar to that shown in Figure 16.

Microcrystalline Colloidal Alumina

Figure 17 is an electron micrograph of "synthetic" colloidal alumina microcrystals (or microfibrils).[7]   Clusters of these microcrystals are shown in Figure 18.   The dimensions of these submicron rodlike and rigid micro-
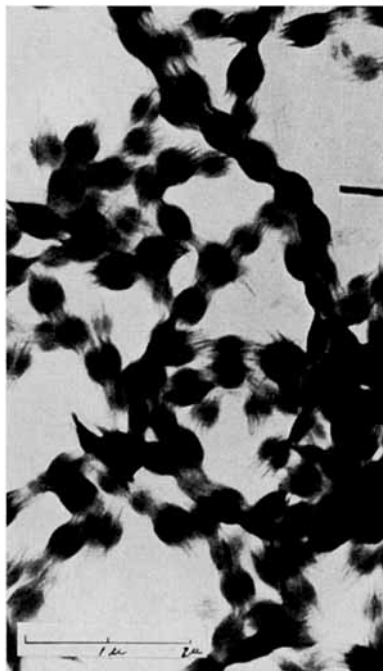

Fig. 18. Formation of relatively organized clusters of colloidal alumina.   12,500×.
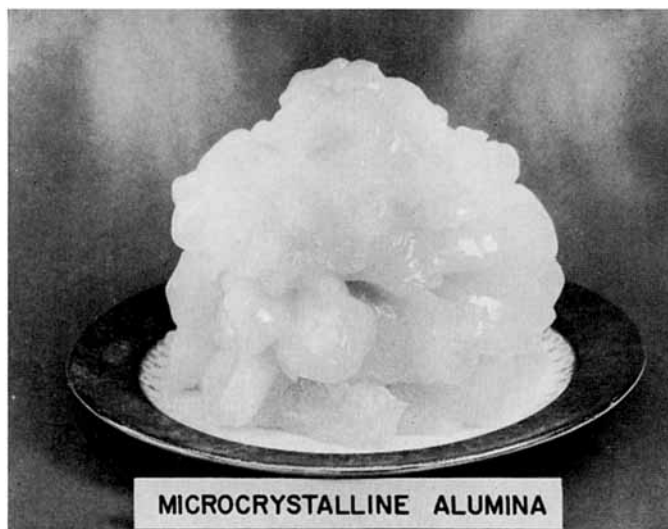

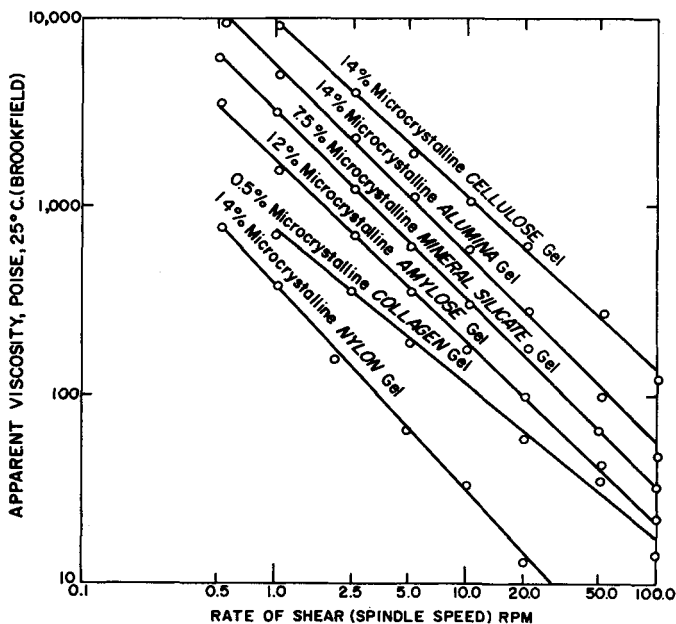Fig. 19. Aqueous microcrystalline alumina gel, 14% solids.

Fig. 20. Viscosities of aqueous microcrystalline gels as the function of increasing rate of shear (log scales).

crystals are of the same order of magnitude as the microcrystals of cellulose, amylose, and chrysotile. In aqueous dispersion, they give a typical stable microcrystalline colloidal gel at 14% solids (Fig. 19).

All of these six microcrystalline polymer materials exhibited novel rheological phenomena. Their gels are highly non-Newtonian, and they exhibit varying degrees of plastic and pseudo-plastic behavior combined with thixotropy. Unlike molecular solutions of polymer materials, the structural gels made from these particles have unusual viscosity stability with time. Figure 20 compares the shear-thinning behavior of all six systems, and the constancy of the slopes for these products in aqueous media is noteworthy. J. Hermans, Jr.[9] has studied the rheology of microcrystalline cellulose gels in considerable detail.

A side-by-side comparison of all six novel colloidal polymer systems in water is shown in Figure 21.

We have endeavored to describe a growing family of colloidal microcrystalline polymer products, of which microcrystalline cellulose was the forerunner. All of them are based on a new and truly colloidal range of macromolecular particles. The rheology, viscosity stability, and other functional properties of these novel materials depend upon the presence of discrete colloidal particles with the composite molecular weight of unit particles in the millions.

The colloidal macromolecular phenomena exhibited by discrete, submicron microcrystalline polymer particles proffer significant opportuni-
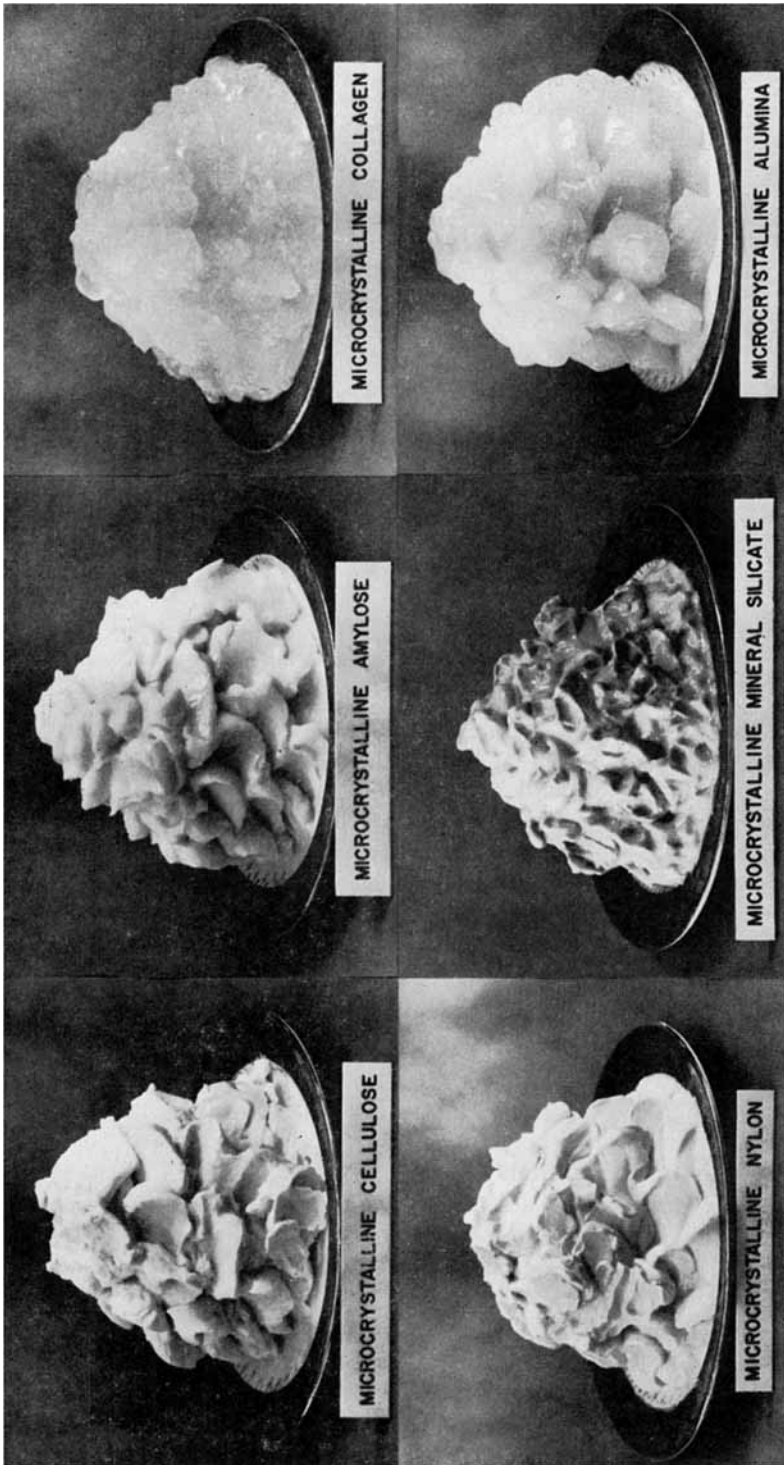
Fig. 21. Microcrystalline gels.

ties for new commercial products possessing useful and novel functional properties.   Our research in this new field of polymer science is continuing.

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Résumé

La cellulose microcristalline colloidale introduite en 1961, est maintenant un produit commercial à succès avec des marchés mondiaux. croissants Ce manuscrit décrit les données principales de notre recherche qui continue pour transformer ce polymère fibreux ou fibrogène en des états physiques microcristallins colloidaux nouveaux sans passer par une phase de solution moléculaire homogène.   De nombreux produits colloidaux microcristallins nouveaux sont décrits au départ de matériaux bruts naturels et synthétiques.   Ils sont comparés pour la première fois.   La cellulose, l'amylose, le collagène, le nylon et les silicates minéraux de chrysotile.   De nombreuses micrographies électroniques non publiées antérieurement sont présentées.   Ces produits démontrent un domaine nouveau croissant de la science des polymères micre cristallins colloidaux. Ils ouvrent de nouvelles possibilités pour des nouveaux produits polymériques basés sur un concept original à savoir, la transformation de monocristaux de polymères au départ de leur réseau naturel ou synthétique et par une énergie mécanique appropriée, leur transformation en microcristaux polymériques colloidaux submicroniques dispersés dans divers liquides de facon à former des systèmes gélifiés uniques ou réagrégés à l'état solides pour former des molécules colloidales poreuses.

Zusammenfassung

Die 1961 eingeführte mikrokristalline Cellulose ist jetzt ein erfolgreiches Handelsprodukt mit zunehmendem weltweiten Markt.   Die vorliegende Mitteilung beschreibt

einige wichtige Befunde aus unseren neueren Arbeiten zur Umwandlung fasriger oder faserbildender Polymersysteme in einen neuen kolloiden mikrokristallinen physikalischen Zustand ohne Durchlaufen einer homogenen molekularen Lösungsphase.   Einige neue mikrokristalline kolloide Produkte aus folgenden natürlichen und synthetischen polymeren Rohstoffen werden zum ersten Male beschrieben und einander gegenübergestellt: Cellulose, Amylose, Collagen, Nylon und Chrysotylmineral-Silikate.   Viele bisher nicht veröffentlichte elektronenmikroskopische Aufnahmen werden gezeigt. Diese Produkte bilden ein neues wachsendes Gebiet der Wissenschaft der kolloiden mikrokristallinen Polymeren.   Sie erschlissen wachsende Möglichkeiten für neue Polymerprodukte, die auf dem ursprünglichen Konzept beruhen, nämlich der Ablösung von Polymermikrokristallen aus ihrem natürlichen oder synthetischen Netzwerk und ihrer darauffolgenden Freisetzung als diskrete submikroskopische, in verschiedenen flussigen Medien unter Bildung einzigartiger Gelsysteme dispergierte Polymermikrokirstalle oder Reaggregierung im trockenen Zustand unter Bildung porenreicher kolloider Teilchen.