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Study of gel formation by ionizing radiation in polypropylene

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ABSTRACT

The objective of this work is to study the formation of microgel in pristine PP and modified PP. The modified PP in pellets was synthesized by gamma irradiation of pristine PP under a crosslinking atmosphere of acetylene in different doses of 5, 12.5 and 20 kGy, followed by thermal treatment for radical recombination and annihilation of the remaining radicals. The gel content of the modified polypropylenes was determined by extraction in boiling xylene for period of 12 h at 138 °C. The gel formed of pristine PP and modified (i.e., irradiated) was characterized using optical microscopy (OM), scanning electron microscopy (SEM), Fourier transformed infrared spectroscopy (FTIR) and X-ray diffraction (XDR). The PP morphological study indicated the microgel formation with increase of spherulitic concentration with dose.

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1. Introduction

The theory of network formation for radical crosslinking copolymerization (RCC) takes into account heterogeneities and microgel formation due to an extensive cyclization and multiple crosslinking. The divinyl monomers can thus be found in macromolecules as units which bear pendant vinyl groups or which are involved in cycles, crosslinks or multiple crosslinks. Since the number of crosslinks necessary for the onset of macrogelation is very low, pendant vinyl groups in RCC are mainly consumed in cycles and multiple crosslinks (Funke et al., 1998).

Intermolecular crosslinking between pendant vinyl groups and radical centers located on different macromolecules produce crosslinks that are responsible for the aggregation of macromolecules, which leads to the formation of a microgel. It must be remembered that both normal and multiple crosslinks may contribute to the rubber elasticity of a network, whereas small cycles are wasted links (Funke et al., 1998).

Microgels are molecular species on the border between normal molecules and particles. Contrary to linear and branched macromolecules, the surface of microgels is rather fixed, thus approaching the characteristics of solid particles. As to their size, it is somewhat difficult to define a limit because the transition from a microgel to a larger polymer particle, e.g. in coarser polymer dispersions, is gradual (Funke et al., 1998).

The common way to investigate the effects of irradiation by either electron beam or γ -rays is to determine the yield of an

event. An event change may involve the measurement of the changes in, for example, molecular weight, solution viscosity or gel content, or the measurement of the amounts of specific gaseous materials evolved during exposure. As stated before one of the main effects of exposure of polymeric materials to high energy radiation is that the material undergoes scission of the main chain and the creation of free radicals, unsaturation (double bonds), crosslinks, and end-linking (Dawes et al., 2007).

Generally the gelation accompanies the formation of three dimensional network structure consisted of crystallinities as a cross-linking point (Hallensleben, 2005). It is reported that some experimental results of the gel-forming crystal provide small differences with bulk-crystallized structure (Nakaoki and Inaji, 2002; Nakaoki and Harada, 2005; Domszy et al., 1986).

One method using gel-type technology for crystallizable polymers, preparing polyethylenes, and including polyethylenes of very high molecular mass and isotactic polypropylene, consists in (without previously preparing polymer solutions) swelling the crystalline polymer films at elevated temperatures in a proper solvent and subsequent precipitation with a non-solvent at different conditions (Andrinova and Pakhomov, 1997).

Results of exposed i-PP (Otaguro et al., 2010) to gamma rays irradiation from 5 to 100 kGy under inert atmosphere showed that gamma irradiation of iPP produce chain scission, branching and crosslinking.

Polypropylene undergoes net crosslinking when exposed to ionizing radiation in the absence of oxygen. Also undergoes significant levels of main-chain scission on irradiation according to studies concerning the understanding of molecular changes

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weight and the rate of gel formation on irradiation (Hill and Whittaker, 2005).

The literature shows (Cheng et al., 2010) a revision of processability improvement of polyolefins through radiation-induced long-chain branching for the purpose of improving melt strength of polypropylene (PP) and polyethylene (PE). Long-chain branching without significant gel content can be created by low dose irradiation of PP or PE under different atmospheres.

The molecular changes produced in polymers by radiation may be classified into: scission and crosslinking of the polymer molecules, leading to decreasing or increasing of molecular weight and the possible development of an insoluble or gel (g) fraction of the polymer above the gel dose, D_g , which increases with dose up to a limit, which depends on the ratio of scission to crosslinking (O'Donnell, 1991).

Many of the physical and chemical properties of gels are determined by the porosity of the underlying molecular network. The build-up of an infinite network and even its existence often depends on irreversible aggregation processes during the earliest stages of structure formation. The results obtained by Kolb (1996), showed change of the structural properties and the cluster size distribution when passing from the aggregation to gelation stage. The measured fractal dimension of the cluster changes continuously as one approaches of the gelation transition (Kolb, 1996).

In other work Meakin (1999), wrote about relationships between aggregation, gelation and spinodal decomposition and about the physical behavior of systems containing fractal aggregates.

Synthesis of nano/microgels by intramolecular crosslinking of individual polymer chains can be also initiated by ionizing radiation. The main advantage of this method is that it can be carried out in a pure polymer/solvent system, free of any monomers, initiators, crosslinkers, or any other additives. The ionizing radiation can be used in the synthesis of polymer gels (both macro and microscopic) in two general ways: either by inducing crosslinking polymerization of monomers or by inducing crosslinking of polymer chains in the absence of monomers. By using ionizing radiation it is possible to obtain a polymer gel starting from mono-functional monomers. More often than not, multi-functional monomers are used anyway, usually in order to increase the yield of cross-linking and thus reduce the radiation dose necessary to produce a gel of a given crosslink density (Ulanski and Rosiak, 2004; Rosiak et al., 2005).

Matsuda et al. (1987) studied the sol-gel transition and the structure of isotactic polypropylene (iPP) gels formed from toluene and o-xylene solutions. The gel melting temperature was measured and its dependency on polymer concentration as well as molecular weight, increased gradually with increasing the polymer concentration. The results showed a somewhat different network structure wherein, containing many spherulites in contact with each other, being bound with crystalline ties. This indicates that these spherulites and crystalline ties form a three-dimensional network structure.

The objective of this work is to study the formation of microgel in pristine PP and irradiation modified PP.

2. Experimental

2.1. Materials and methods

The commercial iPP in pellets was supplied by Braskem. The MFI is 1.5 dg min^{-1} (ASTM D 1238-4), obtained using a Ceast apparatus operating at 230°C with a charge of 2.16 Kg. The acetylene (99.8%) supplied by White-Martins S/A, of Brazil, was used to synthesis of modified polypropylene.

The irradiation of the pellets was performed under acetylene atmosphere in a ^{60}Co gamma source and dose rate of 5 kGy h^{-1} .

The irradiation doses were 5, 12.5 and 20 kGy monitored by a Harwell Red Perspex 4034 dosimeter. After irradiation the pellets samples were submitted to thermal treatment at 90°C for 1 h (Oliani et al., 2010a, 2010b).

2.1.1. Gel fraction/sol fraction

The gel fraction constitutes the insoluble fraction, to be determined after elimination of solvent for drying in the vacuum until constant weigh. The fraction gel is determined by the relation between the mass of the dried gel and the initial mass of the sample multiplied by 100. The gel content was determined by extraction in boiling xylene containing antioxidant Irganox 1010 for period of 12 h at 138°C , ASTM D 2765 2006. The extraction was done involving the sample of PP in a stainless-steel sieve of 500 mesh. The sol fraction, that is, the soluble part of the samples was gotten by the decantation in beaker to the room temperature of 25°C , with the total volatilization of the xylene and gradual deposition of dried material film on fine glass substrates. The initial concentration of the PP for the measure of gel fraction was of approximately $0.1 \text{ g}/100 \text{ cm}^3$.

2.1.2. Optical microscopy

Light microscopy Olympus model BX 51, was used to observe the gel surface at a fixed magnification of 100 times.

2.1.3. Scanning electron microscopy

Scanning electron microscopy was done using an EDAX PHILIPS XL 30. The nonconducting materials, like most of polymers, need to be coated using a metal including silver, gold or gold-palladium, or carbon to their outer surfaces be conductive. In this work, very thick coating of gold is sputter-coated onto the samples.

2.1.4. Fourier transformed infrared spectroscopy

The analyses were performed using attenuation total reflectance accessory (ATR) Smart orbit in the Thermo-Nicolet spectrophotometer, model 380 FT-IR.

2.1.5. X-ray diffraction

X-ray diffraction (XRD) measurements were carried out in the reflection mode on a Rigaku diffractometer Mini Flex II (Tokyo, Japan) operated at 30 kV voltage and a current of 15 mA with $\text{CuK}\alpha$ radiation ($\lambda = 1.541841 \text{ \AA}$).

3. Results and discussion

3.1. Gel fraction

The result of the gel fraction is shown in Table 1.

The values of the gel fraction remained constant in the different doses of irradiation. The obtained gel fraction of

Table 1
Gel content of the samples of pristine PP and modified PP.

Samples	Gel fraction (%)
iPP	1.2
PP 5 kGy	1.0
PP 12.5 kGy	1.3
PP 20 kGy	1.0

approximately one percent is very small and not support the difference observed in the SEM micrographs.

3.2. Optical microscopy

The analysis for optic microscopy with polarized light was carried through the dried sol fraction, that is, the soluble part of the samples that formed a gel film on fine glass substrate for the called Settling process.

The sample presented in Fig. 1(A) shows irregular or imperfect spherulites grown on cooling a 0.1 g/100 cm³ solution of pristine PP in xylene, (Oliani et al., 2012; Khoury, 1966). On the Fig.1(B)–(D), there is a high concentration of spherulites with spherical form achieved in the same manner indicative of the presence of polypropylene microgels.

In similar work Nedkrov, et al. (1991) found spherulites of non irradiated PP in thin film, obtained from solution and in PP irradiated, found aggregates of spherulites with rough surface, grown on thin film.

3.3. Scanning electron microscopy

The visualization of microgels can be realized by various microscopic techniques. More complex microgel structures, multilayers, foils, and surface features of microgel-based materials can be visualized by scanning electron microscopy. SEM enables the analysis of thick, nontransparent sample and due to its large focus depth gives sharp pictures of structurally complex materials, (Ulanski and Rosiak, 2004).

The morphology of the insoluble material which is retained in the 500 mesh stainless-steel sieve after extraction in boiling xylene is presented in Fig. 2. In this material consisting of microgels of PP, Fig. 2(A) are observed some crystals of irregular form while in (B)–(D) the spherical form predominates. These structures are evident in samples irradiated with higher doses (12.5 kGy and 20 kGy).

In the samples deposited on glass substrate, Fig. 3, spherulites with average diameters of 26 μm for pristine, 20 μm for 5 kGy, 15 μm for 12.5 kGy and 12 μm for 20 kGy, respectively. Already in the restrained samples in the steel screen showed a growing increase of the amount of spherical structures with the dose of irradiation is observed. For the determination of the gel fraction, the initial concentration of PP was about of 0.1 g/100 cm³.

In Fig. 3(A) is observed the formation of thin film around a only spherulite, also in Fig. 3B, at low dose the organization of spherulites was also deficient. At (C) and (D), when exposed to higher radiation doses are formed more nucleation points that conduct to spherulites formation and then to microgels.

According to Matsuda et al. (1987), the diameter of the gel depends on the concentration used. In this article reported that concentration between (1–5 g/100cm³) with no gel, polymer was precipitated in the solution and small spherulites with 10–30 μm diameters had been found. Concluding, the diameters and the number of spherulites, gradually enhance with increase of concentration and the diameter of spherulites obtained in gel was of approximately (30–40 μm). The fact is that a tolerable percentage variation exists when working in a lesser concentration, our case, in which we obtained spherulites dimension near to that reported. The irradiation effect is to decrease molar mass with

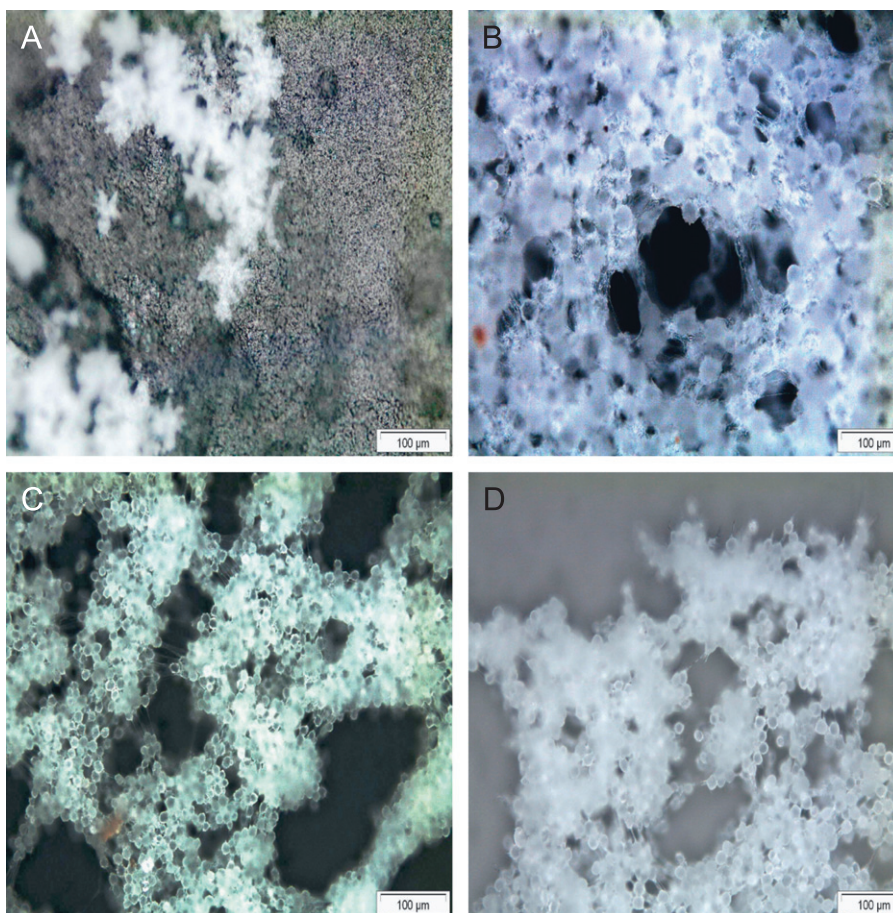


Fig. 1. Photomicrographs obtained by MO of polypropylene gel: (A) Pristine, (B) PP 5 kGy, (C) PP 12.5 kGy and (D) PP 20 kGy, scale=100 μm.

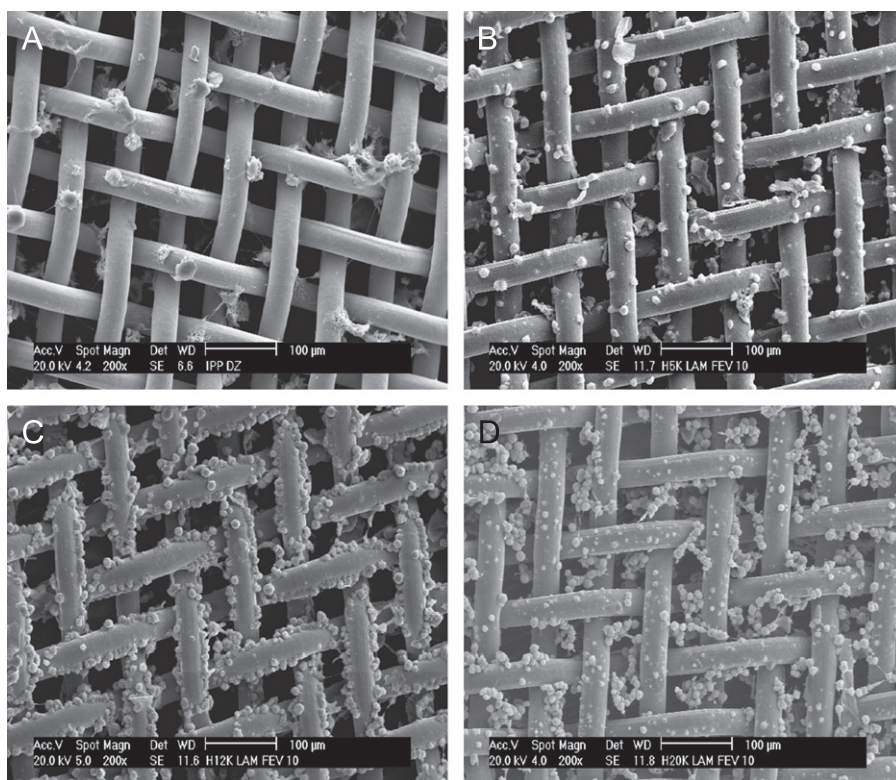


Fig. 2. Gel fraction content in stainless-steel sieve of samples: (A) Pristine, (B) PP 5 kGy, (C) PP 12.5 kGy and (D) PP 20 kGy, scale=100 µm.

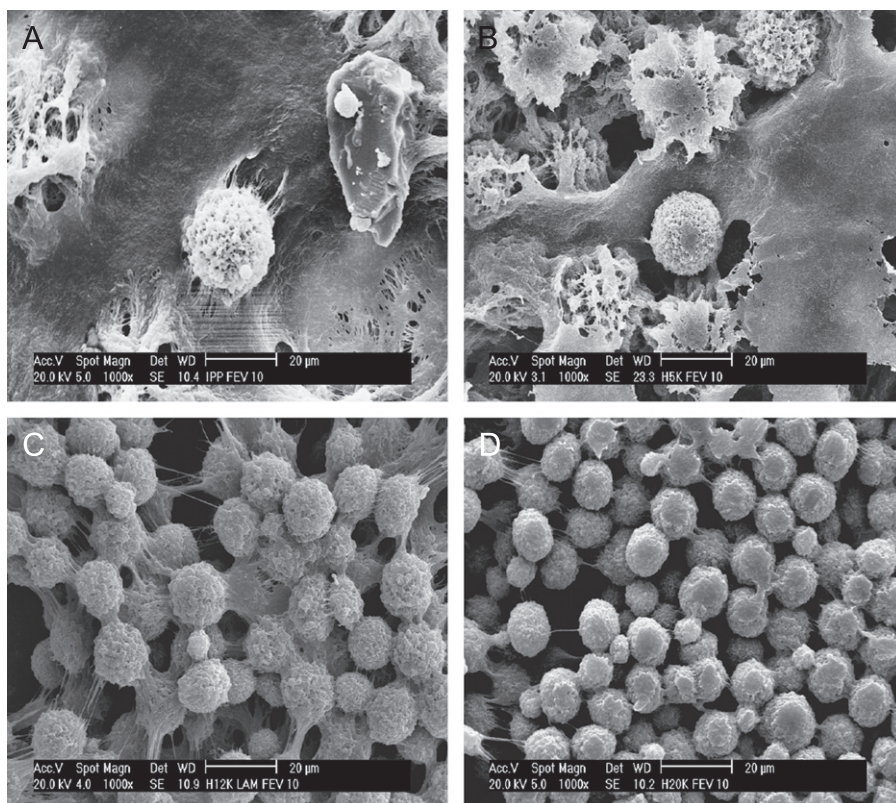


Fig. 3. SEM of the gel from solution crystallized in glass substrate, F_s = soluble fraction: (A) Pristine, (B) PP 5 kGy, (C) PP 12.5 kGy and (D) PP 20 kGy, scale=20 µm.

formation of short segments that incentive the nucleation phenomena. In consequence occurs the formation of molecular structure of spherulites with small dimensions.

The macrochain reactions induced by the gamma irradiation in acetylene promote the formation of crosslinked and degraded structures enhancing chain scission and branching in the

PP structure, (Yoshiga et al., 2009). Branching and crosslinks create nucleation points that forms crystallites or lamellas, considered as nanogels with nucleation effect. The rearrangement of these structures favoring the spherulite formation and organization of microgels is enhanced with radiation dose.

3.4. Fourier transformed infrared spectroscopy

The infra-red spectroscopy, IR, is the versatile method to follow chemical modifications in a polymeric material. Studies carried through by some researchers (Rivaton, et al., 2004; Lemaire, et al., 1996), presented the formation of carboxylic groups with maximum absorption between 1714 cm^{-1} and 1755 cm^{-1} .

The band attributed to stretching of the carboxylic group $\text{C}=\text{O}$, appears in the IR spectrum as an intense band, at around 1740 cm^{-1} , as shown in the Fig. 4. As this band alone appears in the modified samples, it is possible that, the irradiation in acetylene atmosphere allowed the formation of oxidizing group from reactions of scission of chain in consequence of presence of oxygen.

Different from the pristine sample, the spectrum of modified PP showed three peaks absorption at 1233 , 1213 , and 1199 cm^{-1} ,

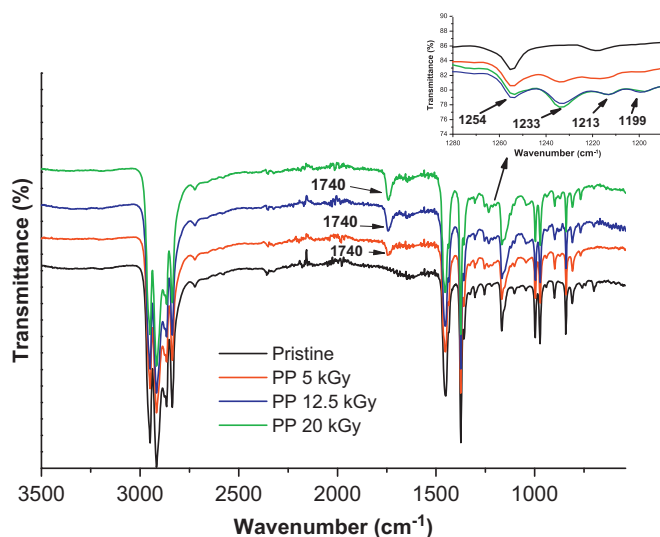


Fig. 4. Illustration of the FTIR-ATR infrared spectra of gel polypropylene.

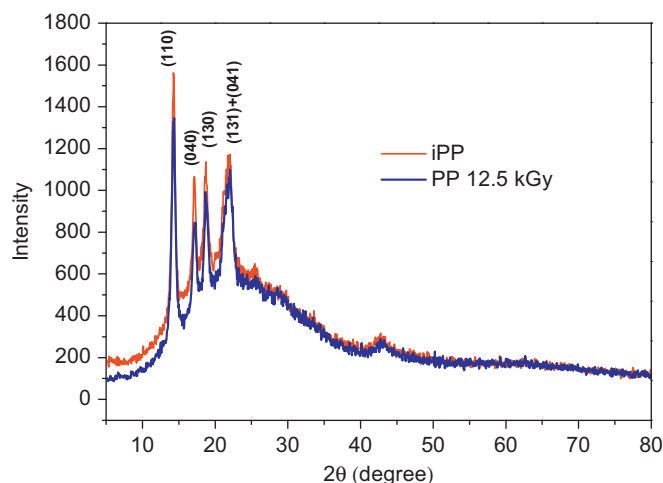


Fig. 5. X-ray diffraction of gel polypropylene and gel PP 12.5 kGy.

respectively. These weak bands have been assigned to the $(=\text{CH}_2)$ deformation mode, attributed to vinyl groups. As described by mechanisms proposed by Jones and Ward (1996) vinyl groups are formed as chain reactions in amorphous phase of PE irradiated in acetylene, and probably are points of nucleation effect.

3.5. X-ray diffraction

In Fig. 5 the X-ray diffraction curves indicate the contribution of the two phases, crystalline and amorphous. The peaks of crystalline phase are identified by their Miller indices and correspond to the α crystalline structure in a monoclinic unit-cell structure ($a=6.66$; $b=20.78$; $c=6.495\text{ \AA}$ and $\beta=99.6^\circ$), according to Burgt (2002).

In X-ray analysis at high diffraction angles, Fig. 5, showed by interplanar distance obtained from these curves: $d_{(110)}=6.28\text{ \AA}$, $d_{(040)}=5.18\text{ \AA}$, $d_{(130)}=4.74\text{ \AA}$ and $d_{(131)+(041)}=4.06\text{ \AA}$.

4. Conclusions

The found spherical structures in this work are microgel of spherulites that if present linked by fibrils constituting the phases amorphous and crystalline. The spherulites and fibrils form a three-dimensional linked structure and its connection if it processes through linkings between crystals.

The main difference between pristine PP and PP modified by irradiation is the spherulites concentration. In pristine PP and 5 kGy PP, the spherulites formation is made difficult by the absence of nuclei in the amorphous phase. On the other hand with the higher dose irradiation, the PP amorphous phase contains formed nuclei due to the branching and crosslinking increasing with the irradiation dose. The microgels observed are spherulites linked by tie molecules.

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