

## Gel in Polyethylene

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### Synopsis

A quantitative test for the presence of gel (insoluble polymer) in polyethylene is described. A number of experiments were performed by using the test and on the polymers separated by the test. It is concluded that gel is crosslinked polyethylene in the form of discrete particles of significant size, the large ones, probably weighing up to at least 10 mg. Some crosslinks are broken by treatment with solvents above 200°C., and much of the gel is thus rendered permanently soluble. Gel is also insoluble in the reaction medium in which it is produced. Thus, even if the ethylene-polyethylene phase relationships would predict a homogeneous reaction, the reaction must be heterogeneous if gel is present. Therefore, kinetic treatments of ethylene polymerization which do not consider phase separation when gel is found in the reaction product are oversimplified.

### INTRODUCTION

It is a recognized fact that material which is insoluble in normal polyethylene solvents is sometimes formed when ethylene is polymerized by free radicals.<sup>1,2</sup> This insoluble portion of the polymer is frequently termed gel.<sup>3</sup> Gel in experimental samples has varied from 0 to 60% by weight of the polymeric product in our experience, and has been reported as high as 70%.<sup>2</sup> In spite of the extent to which gel may be formed, its formation and existence have been completely neglected in recent kinetic or mechanistic descriptions of the polymerization.<sup>4,5</sup> As an outgrowth of a comprehensive study at this laboratory of the polymerization of ethylene, we undertook to determine what gel is and how it is formed.

### EXPERIMENTAL PROCEDURES

#### Analysis for Gel Content

The procedure for determining gel content was based on the principle of extracting the soluble polymer from the whole polymer sample. The insoluble portion was then recovered and weighed. The preferred procedure is as follows.

A piece of Whatman No. 541 filter paper of 15 cm. diameter was cut and folded into an open-ended packet held together with paper clips. The packet, in a weighing bottle, was dried in a vacuum oven at 80°C. for at least 4 hr. and weighed. A small amount of polyethylene (preferably

0.25–0.4 g.) was placed in the packet which was then closed, redried, and reweighed. The packet was placed in a vapor-jacketed Soxhlet extractor (Corning No. 92150) and extracted with refluxing solvent. Unless otherwise specified, the solvent was a commercial xylene mixture and the extraction time was 48 hr. At the end of this extraction period, the sample was extracted (in the same apparatus) for 4 hr. with methanol to remove the solvent. The packet was then dried for approximately 16 hr. and weighed to obtain the net weight of material which was not extracted (gel). These drying times were sufficient to produce specimens of constant weight. The overall reproducibility of this technique on blank packets was about  $\pm 0.2\%$ .

### Batch Polymerization

The reactor and polymerization procedures have been described.<sup>6</sup>

### Continuous Polymerization

Continuous runs were made in a 4-m. long tubular reactor of 8 mm. internal diameter which was immersed in an oil bath. Ethylene and other feed constituents were mixed and fed to the reactor at a rate of 2–4 kg./hr. An automatic, pneumatically operated valve continuously discharged the contents of the reactor to atmospheric pressure under an inert atmosphere in such a way that the polymer separated from the gas as a powder or fluff which was collected.

## RESULTS

### Gel Analysis

This section deals with the gel-measuring method just described and experiments performed to develop it.

The effect of sample size on the results was investigated using different amounts of the same polymer made by continuous polymerization. The results of a 24-hr. extraction, plotted on logarithmic probability coordinates in Figure 1, show a correlation between sample size and per cent polymer retained in the packet. This is reasonable because the removal of soluble polymer depends on the passage of polymer solution through the filter paper. Rate of passage depends on the ratio of paper area to polymer weight, on the proportion of pores that become plugged with swollen material, and on the viscosity of the polymer solution. Increasing sample size at constant packet size makes all three factors less favorable for extraction.

The effect of the duration of the extraction was studied with the use of ten samples of another continuous reactor polymer and xylene as the solvent. Some of the samples were removed, the gel level recorded, and the sample replaced in the extractor and the extraction resumed. The data are shown in Table I.

TABLE I  
Summary of Time Study Data

Time, hr.	Material not extracted, wt.-%									
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
16									40.2	37.6
24							30.9	27.9		
32									35.0	32.7
48					29.4	26.1	26.8	24.9	32.0	26.9
64									28.7	24.5
72			24.4	22.7			25.3	23.8		
80									28.9	24.5
96	21.2	23.1	23.8	21.7	24.7	21.9	24.7	22.7	27.1	23.3
120	Broken	23.4	24.0	21.8	Broken	Broken	23.2?	21.9?	23.8?	20.8?

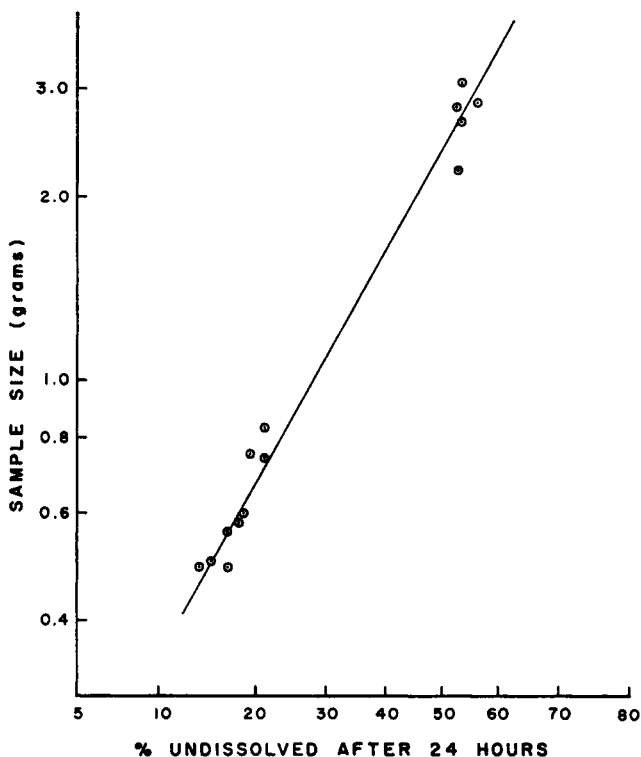


Fig. 1. Effect of sample size on apparent amount of insolubles.

After 96 hr., the filter paper packets began to deteriorate rapidly. Thus, some of the data collected at 120 hr. are questionable because the packets may not have been polymer-tight. Other data were lost because the packets broke open.

Of importance both to the test and to an understanding of the nature of gel is the effect of changing the extraction solvent. Extractions with various solvents were carried out in a nitrogen atmosphere to eliminate possible oxidation at high temperatures. These data are summarized in Table II. Data on diethylbenzene extractions could not be obtained after 24 hr. due to decomposition of the paper packets.

TABLE II  
Effect of Extraction Solvent

Solvent	Boiling point, °C.	Gel, %				
		After 24 hr.	After 48 hr.	After 72 hr.	After 96 hr.	After 144 hr.
Benzene	81	46.2	29.6	27.0	26.7	26.3
Toluene	110	41.3	23.8	20.9	20.2	20.4
Xylene	138	35.2	23.9	21.0	20.6	20.4
Diethylbenzene	181	28.4	—	—	—	—

From the data in Tables I and II we have drawn the following conclusions. There is no detectable difference in the gel level whether the extraction is stopped and restarted or whether the extraction is run continuously for the time specified as long as the packet pores do not plug. Extraction is more rapid with higher-boiling solvents, but after long times essentially the same gel values are found regardless of solvent. With xylene and toluene, extraction is nearly complete after 48 hr. and fully complete after 96 hr.

To circumvent the difficulty of packet deterioration at high temperatures, a metallic filter of 40  $\mu$  pore size was substituted for the paper which had a pore size of 4.8  $\mu$ . Table III shows that, with xylene, identical results are obtained with both the filter and the packets. When the xylene-insoluble material was further extracted with diethylbenzene and then with  $\alpha$ -chloronaphthalene, b.p. 236°C., more material dissolved. This dissolved polymer which had been insoluble was now completely soluble in hot xylene. This experiment shows two things. First, an irreversible change took place which rendered a portion of the insoluble material soluble. Second, gel must exist in the form of particles essentially none of which, when swollen with solvent, have a diameter of less than 40  $\mu$ .

TABLE III  
High-Temperature Extraction Study

Treatment	Gel, %	
	Metallic filter	Paper packet
Xylene, 48 hr.	23.5	22.4, 24.1
Above, then diethylbenzene, 24 hr.	17.8	
Above, then $\alpha$ -chloronaphthalene, 24 hr.	2.7	

It can be seen from the data in Table I that, when repetitive experiments were made, the sample-to-sample variation in per cent gel exceeded the experimental error of the method. This point was investigated further by subjecting 10 samples of another continuous reactor polymer to the xylene extraction test. The data are given in Table IV with the samples arranged in increasing order of per cent gel found at the end of the experiment. It is seen that the results scatter badly, and that a normal distribution, which would be expected from strictly random errors in the analytical procedure, is not followed. At the end of this experiment, the packets were carefully examined for holes (none were found) and opened for a visual inspection which qualitatively confirmed the data in Table IV. Thus, although the gel value on any given subgram portion of a polymer can be quite precisely obtained, great caution must be exercised in making statements about the whole polymer from just one datum. It is concluded that gel is not homogeneously distributed in these samples.

TABLE IV  
Results of a Replicated Gel Determination

Sample	Gel, wt.-%
10	0.20
1	0.21
7	0.48
6	0.65
5	0.71
8	1.43
3	1.96
2	2.74
4	3.69
9	5.61

Because of the variation of gel contents within these polymers, additional precision in the method can only come by taking the sample from the polymer in such a way that it is more representative of the whole polymer. A number of different sampling techniques were tried, pellets, powder, and reprecipitated material being used without significant reduction in the sample-to-sample variation. Attempts to use larger sample sizes failed because of incomplete extraction as previously discussed. Our inability to improve the sampling indicates that at least some of the gel particles are of such size that the presence or absence of a particle makes a significant difference in the results. This means that, for the variations seen herein, these large particles could weigh 10 mg. (dry weight) or more.

### Studies on Gel and Sol

A portion of isolated gel was placed in the optical bomb described by Ehrlich and Kurpen<sup>7</sup> and subjected to butane at 495 atm. and 110°C. and ethylene at 1800 atm. and 185°C. Both conditions are well above the critical solution conditions for polyethylene in these gases.<sup>7,8</sup> In both instances, the gel remained as discrete, mobile, highly swollen particles of a density greater than that of the compressed gas. Very important was the absence of critical scattering on reduction of pressure indicating the total absence of soluble polymer.

This gel was practically infusible and had no observable melt flow at 190°C. Its infrared spectrum was identical to that of the whole polymer from which it was separated. The soluble polymer, recovered by methanol precipitation from the extractant liquors, had a greater melt flow than the whole polymer containing gel.

These results indicate that gel is polyethylene of very high molecular weight and corroborate the conclusion that gel is insoluble in all solvents.

### Experiments Producing Gel

During the course of our batch polymerization experiments, it was observed that some polymerization additives always caused gel to be

TABLE V  
Gel Formation Study

	Dow P-400 polyglycol	Glucose syrup	Glycerine	Ethylene glycol	1,2- Propanediol	1,3- Propanediol	Pentol
Gel formed on reactor wall	Yes	Yes	Yes	No	No	No	No
Gel present in polymer	Yes	Yes	Yes	Yes	Yes	Yes	No
Gel in polymer, %	—	—	—	5.5	2.3	2.0	—
Measured $C_s$ /estimated $C_s$	—	—	0.15	0.20	0.55	0.50	—

formed. Table V summarizes briefly the results from a series of experiments made to determine what types of compounds are gel formers. The possibility that gel forms as a result of very high viscosities in the reaction was investigated by adding pentol, a hydrocarbon oil of viscosity approaching that of Dow's polyglycol or glucose syrup. This possibility was discarded when pentol was found not to cause gel. It was noted that all of the compounds which invariably formed gel are highly hydroxylated. The presence of hydroxyl groups alone could not be responsible for gel formation, however, because alcohols were found not to cause gel. Chain transfer constants were measured for some of the compounds using our standard procedures<sup>6</sup> and compared to the chain transfer constant which would be expected by analogy with compounds for which the chain transfer constant is known.<sup>6,9</sup> It is seen that the measured chain transfer constants are all less than the estimated values. Although this is in the nature of indirect evidence, it appears that these highly hydroxylated substances are not completely in solution in the reaction medium. In other words, part of the material added to the polymerization has apparently formed a second phase which is immiscible with the bulk of the polymerization.

## DISCUSSION

The facts that gel (1) seems to be chemically polyethylene, (2) has very high apparent molecular weight, and (3) is totally insoluble in all polyethylene solvents up to at least 180°C. indicates that it must be crosslinked polyethylene. It is surprising, however, that some of the crosslinks seem to be easily broken above 200°C., but perhaps the swelling action of good solvents at these temperatures is sufficient to rupture some bonds. The consistent formation of gel in a reactor where a second phase has been established by addition of an insoluble or semisoluble material indicates that gel must be formed either in a monomer-poor second phase where intermolecular chain transfer and crosslinking would be favored or at an interface or both.

The reactor wall itself presents a type of interface. In this context, it is noteworthy that gel occasionally was found adhering to the wall (see Table V) so tightly that it was removable only by vigorous mechanical action. The variation in gel content between small samples taken from a single polymer is consistent with a postulate of gel being formed at the reactor wall and being swept out of the reactor sporadically. However, the frequent preparation of gel-free polymers under some polymerization conditions argues that the reactor wall is not a gel-forming interface in and of itself. The instances cited in Table V, where the reactor walls were clean but gel appeared in the product, also support this conclusion. Thus, it appears that the reactor wall, and perhaps other interfaces, are neither necessary nor sufficient to cause gel formation. The apparent involvement of the wall in some experiments is probably due to the occurrence of gel-forming conditions at a wall site.



Since it is known that polyethylene can be crosslinked by peroxides, it is attractive to propose that gel is formed by attack of free radicals on polyethylene chains which are in a polymer-rich, monomer-poor phase where crosslinking would be favored. As long as conditions are such that a substantial proportion of the incipient gel particles grow to significant size, all analytical results can be accounted for. However, we have run a number of polymerizations in the batch reactor at conditions where the polymer must separate into such a second phase<sup>8</sup> and have not observed gel in the polymer, although after many such runs the reactor wall was noticed to be covered with a thin, discolored film of insoluble polymer. Since gel itself is insoluble in ethylene, a second phase consisting of swollen polymer must exist once gel is formed. Possibly gel formation is accelerated after the first gel is formed because of the increased amount of the second phase. This possibility suggests that there is a pseudo induction period before gel appears in detectable amounts. These concepts could account for the apparent absence of gel in short batch runs where the reactor is cleaned after each run and would also suggest that gel should be more noticeable, for the same polymerization conditions, in the effluent of continuous reactors (which achieve a sort of dynamic steady state) than batch reactors. Indeed, this has been our observation.

The results of this study are in general accord with an optical study of gel particles in polyethylene with one exception. The upper limit on the size of these particles was previously stated to be  $20\ \mu$ , and particles ranging in size down to  $0.5\ \mu$  were also observed.<sup>10</sup> However, this optical study was carried out on commercial polymers which, we may safely assume, had been passed through an extruder and its protective screen. Since the gel particles were described as readily friable, it is likely that the larger particles which we observed were broken down into the smaller particles which Bryant et al. observed by the shearing action of commercial processing equipment and thus their particle sizes do not represent the range of particle sizes formed in the reactor.

## CONCLUSIONS

On the basis of the evidence at hand, it appears that some polyethylene can become crosslinked during the polymerization process. The formation of this crosslinked material or gel is enhanced by phase separation in the reactor. The gel which exits from the reactor is in the form of discreet particles of perhaps up to 10 mg. in weight. Because of the large size of the particles, subgram samples of a whole polymer will only roughly approximate the composition of the polymer. Some of the crosslinks can be broken by treatment with solvents above  $200^{\circ}\text{C}$ . rendering much of the gel permanently soluble.

Kinetic treatment of the free-radical polymerization of ethylene probably does not require additional steps to account for the formation of crosslinked material since the gel probably results from a combination of chain-transfer (to polymer) and termination steps already included in the kinetic analysis.<sup>1</sup>

However, regardless of the polymerization conditions, the reactor will be in a two-phase condition when gel is present. Therefore, when gel is present, a kinetic treatment assuming a homogeneous reaction should be applied with extreme caution if at all.

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