Ultrasonic Degradation of the Gel Phase in Impact Polystyrenes

ERIC R. WAGNER and ROBERT J. COTTER,

Union Carbide Corporation, Bound Brook, New Jersey 08805

Synopsis

The rupture of the crosslinked rubber membranes in the gel particles of impact polystyrene by ultrasonic energy has been discovered to be a novel route for the semiquantitative analysis of the grafted and occluded polystyrene of the composite. Applying this new technique, the weight-average molecular weight of the matrix, grafted, and occluded polystyrene of a bulk-polymerized impact polystyrene was found to be approximately the same.

INTRODUCTION

Recent electron micrographs[1] of thin layers of bulk-polymerized, polybutadiene-based impact polystyrene (IPS) reveal that the individual gel particles consist of 70–400-angstrom-thick rubber membranes containing many occlusions of polystyrene. The rubber membranes have been grafted[2] with polystyrene and crosslinked during the preparation of the resin. Since the graft polymer in IPS has the dual function of an emulsifier in the soluble form[3] and as an adhesion promoter[4] in the final product, quantitative data for the true graft polymer content in the resin is of importance. However, no known method differentiates between the grafted and occluded portion of polystyrene in the gels. It is assumed that the crosslinked nature of the rubbery network in the membrane hinders separation of the occluded polystyrene by diffusion processes.

Microscopic inspection of the gels of IPS which had been exposed to macromechanical forces, such as in a two-roll mill, revealed that some membranes of the microgels were ruptured and the occluded polystyrene could be washed out with butanone-2. Therefore, ultrasonic energy was investigated for the rupture of the rubber membranes to determine its efficiency.

EXPERIMENTAL

Separation of the Gel Phase of IPS

Solvent Screening Procedure. Commercial bulk-polymerized IPS, 1.00 g, was mildly shaken in 100 ml of various solvents for polystyrene or both polystyrene and polybutadiene, for a given time–temperature cycle. The insoluble gel phase of the resin was recovered by centrifugation at 12,000 rpm, or by filtration through a preweighed amount of filter aid.

Preparative Separations of the Gel Phase of IPS.   In order to collect about 2–3 g of gel from an IPS sample by butanone-2:acetone separation, place 12–15 g of the resin sample and 200 ml of solvent (butanone-2:acetone, 1:1 by volume) in a 500-ml Erlenmeyer flask.   Stopper and stir magnetically for 4 hr.   Pour into four stainless-steel centrifuge thimbles and centrifuge for 2 hr at 12,000 rpm.   Decant the supernatant liquid.   Spread the wet cakes in a thin layer on a Teflon film using a few milliliters of butanone-2 to rinse each thimble.   Allow it to stand at room temperature for 1 hr.   Strip off the remaining solvent in a vacuum oven at 80°C/30 mm Hg for 2 hr.   A paper-like web of gels will be obtained.

Rate of Diffusion of PS through Crosslinked Membranes of Natural Rubber

Homopolystyrene, 25.0 g (or 20.0 g of finely cut polybutadiene), was placed in a 3-in. rubber balloon.   The balloon was evacuated, sealed, and inserted into a pint jar full of benzene.   The benzene outside of the balloon was checked daily for polymer by adding a 2-ml sample to 15 ml methanol.   The amount of benzene withdrawn was replenished with fresh benzene.   The results of this study are described in the discussion section.

Ultrasonic Rupture of Gel Particles

Weigh 1.000 g dry gel into a stainless steel centrifuge thimble.   Add 25 ml benzene and stopper with a rubber stopper wrapped in aluminum foil.   Agitate the shaker at medium speed for 4 hr.   Clamp the thimble in a beaker of ice water and stir with a magnetic stirrer.   Use the regular horn with the Sonifier and insert it into the thimble so that it is ~5 mm below the surface of the liquid.   Sonify (Ultrasonifier Branson-W-185-C, Ultrasonics, Inc., Plainview, New York 11803) at 70 watts for 1.0 hr.   Remove water from the beaker and add ice every 10–15 min.   After 1 hr, turn the Sonifier off and raise the horn out of the liquid.   Rinse thoroughly with benzene so that any gel on the horn is washed back into the thimble.   A drop of the dark brown liquid slurry, when examined microscopically, shows that disruption of the gel particles has taken place.   Slowly evaporate the benzene on a water bath at 75°C.   Remove from the heat and add 30 ml butanone-2:acetone (1:1 by volume).   Stopper and agitate gently on the shaker for 30 min.   Balance the thimbles and centrifuge for 2 hr at 12,000 rpm.   Decant the supernatant liquid, which is faint yellow, but clear.   Save the decanted supernatant solution which contains polystyrene that was formerly occluded for quantitative recovery and analysis.   Dry the disrupted gel remnants in a vacuum oven at 80°C under 5 in. vacuum overnight.   Raise the oven temperature to 150°C for $1/2$ hr, then cool under vacuum.   Reweigh the thimbles containing dry gel.

Recovery of Occluded Polystyrene

Precipitate the decanted supernatant solution of formerly occluded polystyrene into 100 ml methanol with stirring.   Allow to settle overnight and recover quantitatively by filtration through a fritted glass filter.

Analysis of Sonified Gel for Grafted Polystyrene

The amount of polystyrene that is actually grafted to the rubber was determined by the oxidative degradation of the sonified gel with *t*-butyl hydroperoxide/osmium tetroxide.[5]

Molecular Weight Distributions of Matrix, Grafted, and Occluded Polystyrene

Characterization of the three polystyrene fractions was accomplished using gel permeation-chromatographic techniques.[6]

RESULTS AND DISCUSSION

Diffusion of Polystyrene Through Polymeric Membranes

Transport of occluded PS through the rubber membranes which form the phase boundaries of the gel particles necessitates mass transport of solvated macromolecules through polymeric membranes.   As can be estimated from Figure 1, polystyrene molecules that reside in the center of such a cellular rubbery network must pass through up to ten diffusion barriers.

Solubility considerations suggest using a solvent for both PS and polybutadiene as a vehicle for the diffusion of the occluded PS molecules. Benzene, toluene, or chloroform can dissolve the matrix polystyrene and diffuse through the rubbery membranes into the individual gel particle
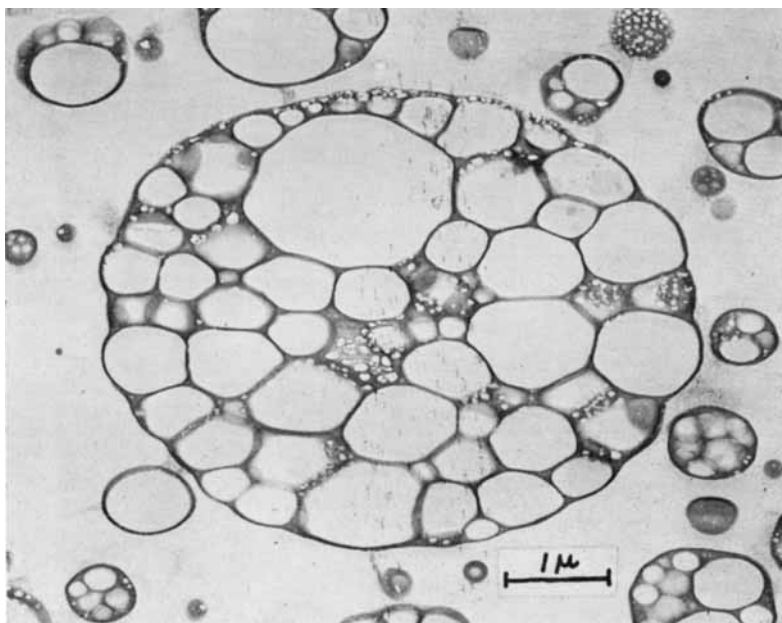

Fig. 1. Rubber membrane structure of impact polystyrene (6% polybutadiene, 22% rubber phase volume); 15000×.

and swell it. The degree of swelling depends on the solubility parameter of the solvent and polymers and on the crosslinking density of the gel. The latter is a function of the process history (thermal or peroxide initiated) of the particular IPS resin sample. The relative degrees of swelling for the gel from a given IPS sample are compiled in Table I. Benzene and chloroform which possess solubility parameters[7] closest to those of polystyrene $[\delta = 9.10 \text{ (cal/sec)}^{1/2}]$ and polybutadiene $[\delta = 8.00 \text{ (cal/sec)}^{1/2}]$ cause the largest degree of swelling.

Direct measurement of the amount of PB–PS graft polymer via solvent extraction of the occluded polystyrene was attempted. Solvents, temperature, and time were investigated. Surprisingly, the data in Table II demonstrate that the quantity of insoluble gel remained essentially constant, and practically no transport of PS through the membranes of the gels took place.

In related experiments, polystyrene pellets or small pieces of polybutadiene rubber (PB) were placed in balloons of crosslinked natural rubber (swelling index $Q_{B_2} = 6$) which were immersed in benzene. Although 350 g benzene diffused into each of the balloons during 600 hr at ambient temperatures, neither PS nor PB was found outside of the membrane. Finally, the osmotic pressure ruptured the balloons. The fact that PB rubber, which has a solubility parameter similar to that of polyisoprene, did not diffuse through the balloon suggests that the barrier characteristics of the rubber membrane stem from geometric factors. That is, the crosslinking

TABLE I

Solvent	Solubility parameter, $(cal/sec)^{1/2}$	Average swollen gel diam.,[a] μ
Butanone-2:acetone	9.52	1.0
Butanone-2	9.45	1.5
Benzene	9.16	2.0
Chloroform	9.10	3.5

[a] Phase microscope, 400×, 10 min of swelling. Original average dry gel diameter 0.5 μ.

TABLE II

Solvent	Time, hr	Temp., °C	Gel,[a] %
Benzene	2.9	26°	23.0
Benzene	16.0	26°	22.5
Benzene	216	78°	21.6
Toluene	16	26°	22.0
Chloroform	16	64°	22.0
Chloroform	216	64°	21.2
Butanone-2:acetone	3.5	26°	22.6
o-Dichlorobenzene	16	180°	19.0

[a] Swelling index Q (toluene), 11.0.

density controls permeation rather than entropic polymer–polymer repulsions.

The rupture of the gels of IPS by osmotic pressure similar to the rupture of the balloons did not occur even when a sample (Q = 11.0 toluene) was dispersed in chloroform for six months. Only traces of PS were found in the chloroform. The lack of diffusion of PS through the PB–PS graft polymer membrane of the gel strongly suggests that the grafted polystyrene chains are not physically entangled in the membrane, but are pendant from the plane of crosslinked polybutadiene molecules. If the grafted polystyrene chains were physically entangled in the membrane, they might facilitate the diffusion of the occluded PS.

Ultrasonic Rupture of Rubber Membranes

The efficiency of ultrasonic energy for the rupture of gel particles was checked by dispersing ∼1.0 g IPS (Fig. 2) in 25 ml butanone-2, benzene, toluene, or chloroform and sonifying the slurry at increasing power for several hours. The amplitude of the ultrasonic energy in the liquid exceeded that cavitation level[8] which is essential for the micromechanical degradation or organic compounds.[9,10] The minimum force to produce velocities in a liquid high enough to rupture carbon–carbon bonds has been calculated as 5.6×10^{-4} dynes.[11]

Inspection of the sonified gel with a phase microscope showed no disruption when butanone-2 was used as the solvent. Sonified gels dispersed in solvents for both PS and polybutadiene and which impart maximum swell-
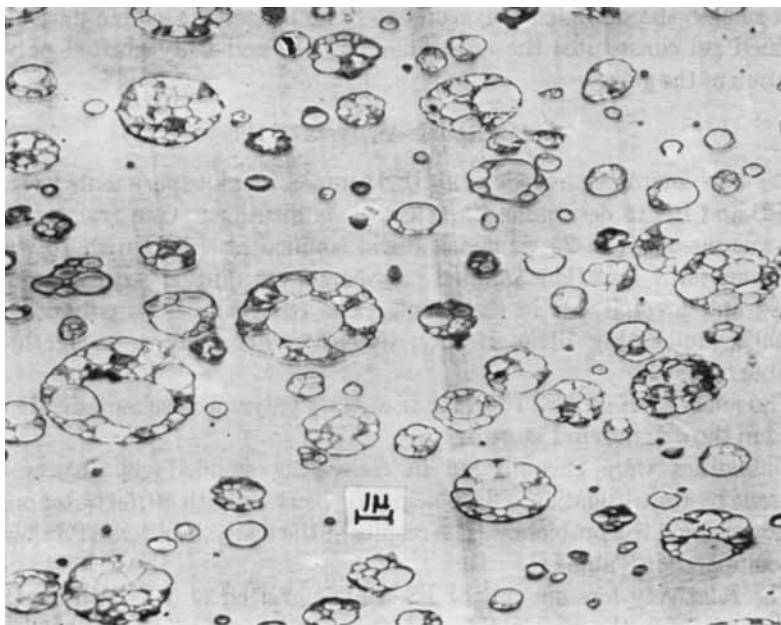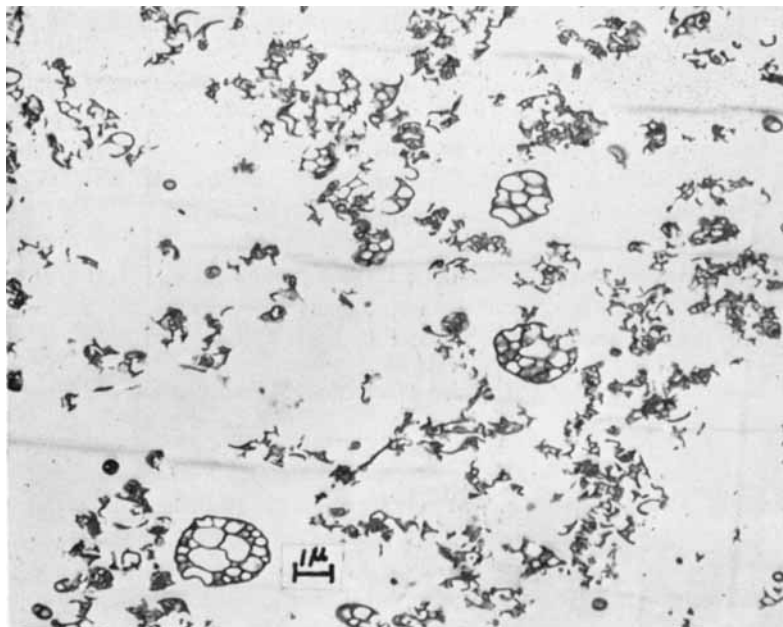

Fig. 2. Microgel of resin B before sonification; 4500×.

Fig. 3. Microgel of resin B after sonification; 5000×.

ing to the membranes were completely ruptured at a power input of 0.56 watts/mm² in 1 hr. Ruptured microgels are illustrated in Figure 3. This electron micrograph shows that the vast majority of the ruptured gels can now release the occluded polystyrene. The benzene-insoluble part of the sonified gel constitutes the crosslinked rubber and truly grafted polymer fraction of the gels.

Quantitative Analysis of IPS

Prior to complete analysis of an IPS sample, blank experiments were run on PS and PB to determine the effect of sonification. One gram of PS or PB was dissolved in 25 ml benzene and sonified at +3°C with 70 watts/ 1.26 cm² for 1 hr. The sonified polymers were diluted with benzene to ~1% and precipitated in methanol. The recovery of the polymers was 98–99%, indicating little, if any, extensive degradation to methanol-soluble molecules.

The analysis of an IPS resin for true graft polymer is schematically outlined in the diagram in Figure 4.

Difficulties were encountered in recovering sonified gel dispersed in benzene by centrifugation. Replacing the benzene with 50:50 butanone-2: acetone solved the problem. The results of the analysis of two IPS samples are compared in Table III.

The relatively low amount of PS that is grafted onto the rubber is in agreement with the area ratio of R:PS occlusions that are visible in the electron micrograph of the unsonified gel of a similar IPS resin in Figure 1.

IPS Sample

Butanone-2 : Acetone Treatment

(followed by)

SOLUBLE (in ◄————————— Centrifugation ————————► INSOLUBLE (in
Butanone-2 : Acetone)   Butanone-2 : Acetone)

MATRIX-PS   GEL
    Isolate by Methanol
    Coagulation and   Slurry with benzene.
    characterize by GPC.   Sonification; strip
                                                              benzene. Reslurry
                                                              with Butanone-2:
ADDITIVES   Acetone. Centrifugation.
    Isolate from Methanol/
    Butanone-2/Acetone
    supernatant.   INSOLUBLE   SOLUBLE
                                            PB-PS graft   Occluded PS
                                                                                              Characterize
                                                                                              by GPC
                                            oxidized

                                            BOUND PS
                                            Soluble
                                            Characterize
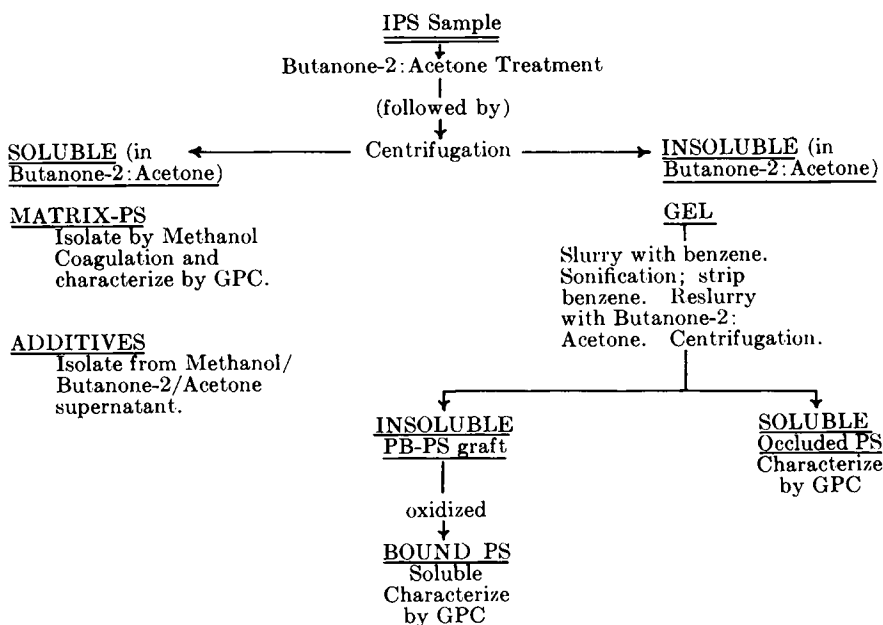   by GPC

Fig. 4.   IPS-Analysis Diagram.

(See also Fig. 2 in ref. 12).   The composition of the gel of the two IPS
samples in per cent and as parts of total resin is shown in Table IV.

If we relate the amount of grafted PS to the rubber in each composite, we
find 25% in resin A and 19% in resin B.   Hence, both composites exhibit
about the same grafting density, and the higher amounts of occluded PS
in the gel of resin B was caused by other factors[13] than the concentration of
PB–PS graft polymer.   It is seen that as little as 6 parts of grafted PS per
100 parts of the gel function as emulsifier and promote adhesion between
the gel particles and the glassy matrix PS in this IPS resin.

Information concerning the weight-average molecular weight of the
matrix, occluded, and grafted PS in IPS has long been sought.   Now, the
ultrasonic gel disruption technique allows one to characterize these three
different types of PS as shown in Table V.

The effects of ultrasonic energy on polymer solutions, specifically on PS,
was studied by several authors.[9,10,14]   Opinions differ on where the chain
breaks, and range from rupture at the center to an absolutely random affair.
Rupture of polystyrene bound to polybutadiene will lower the amount of
true PB–PS graft polymer and increase the amount of occluded PS.   The
data for true graft polymer in resin A and resin B are therefore considered
to be somewhat on the low side.

The expected reduction in the $\bar{M}_w$ of PS after ultrasonic treatment is
apparent on comparing the unsonified and sonified matrix PS.   *The basis
of our analysis of the properties of gel phase polystyrene is the data for the soni-
fied matrix polystyrene.*   The matrix of the IPS sample was separated from

TABLE III

	Resin A	Resin B
Impact polystyrene		
R in IPS, %	13.5	6.4
PS in IPS, %	84.5	91.1
Additives in IPS, %	2.0	2.5
Gel in IPS, %	21.8	21.0
Rubber phase increase,[a] %	63	228
Original Gel		
R in gel, %	62.0	30.2
PS in gel, %	38.0	69.8
Sonified Gel		
Graft polymer in gel, %	77.7	36.2
PS occluded in gel, %	22.3	63.8
PS grafted on R,[b] %	25.2	19.7
Grafting efficiency[c]	4.1	1.3

[a] Rubber phase increase $= \dfrac{\%\text{gel} - \%\text{R}}{\%\text{R}} \times 100\%$.

[b] PS grafted on rubber $= \dfrac{\%\text{sonified gel} - \%\text{R in gel}}{\%\text{R in gel}} \times 100\%$.

[c] Grafting efficiency $= \dfrac{\text{wt grafted PS}}{\text{wt total PS}} \times 100\%$.

TABLE IV

	Resin A		Resin B	
	IPS, %	Gel, %	IPS, %	Gel, %
Rubber	13.5	62.0	6.4	30.2
Occluded PS	4.9	22.3	13.4	63.8
Bound PS	3.4	15.7	1.2	6.0

TABLE V

PS	Resin A		Resin B	
	$\bar{M}_w$[a]	$\bar{M}_n$[a]	$\bar{M}_w$	$\bar{M}_n$
Matrix, as is	256,000	80,000	227,000	51,000
Matrix, sonified	122,000	56,000	80,000	32,000
Occluded PS, sonified	94,000	36,000	104,000	41,000
Bound PS, sonified and oxidized	101,000	18,000	75,000	25,000

[a] The limit of accuracy of GPC is $\pm 10\%$ for both $\bar{M}_w$ and $\bar{M}_n$ data.

the gel phase, reclaimed, and sonified in benzene. The data on occluded and grafted PS were obtained from the sonified gel only. Sonified matrix and sonified occluded PS show within the experimental limits of the GPC technique the same $\bar{M}_w$ and $\bar{M}_n$; hence the occluded polystyrene possessed a molecular weight similar to that of the matrix PS. The data for the

grafted PS indicate a slightly lower $\bar{M}_n$, probably because this fraction was not only sonified but also subjected to oxidation. A comparison of all GPC data leads to the conclusion that the matrix, occluded, and grafted PS of bulk-polymerized IPS resins are of the same magnitude. This is consistent with the known low chain-transfer constant of polybutadiene toward styryl radicals ($C_{tr} = 11 \times 10^{-4}/140°C$) and the low degrees of true grafting found in our analysis.

CONCLUSIONS

The ultrasonic rupture of the membranes of the gels of bulk-polymerized, polybutadiene-based impact polystyrene releases the occluded PS, and facilitates analysis of the true PB–PS graft polymer in impact polystyrene resins.

References

1. K. J. Kato, *Electron Microscopy*, **14**, 220 (1965).
2. F. M. Merrett, Simposio Intern. Chim. Macromol., Milano, Italy, 1954, p. 279.
3. G. E. Molau, *J. Polym. Sci. A*, **3**, 1267 (1965).
4. L. H. Lee, *ACS Preprints*, **27**, 68 (1967).
5. I. M. Kolthoff, *J. Polym. Sci.*, **1**, 428 (1946).
6. J. C. Moore, *J. Polym. Sci. A*, **2**, 835 (1964).
7. K. L. Hoy, *Tables of Solubility Parameters*, Union Carbide Corp., 1968.
8. N. H. Langston, and P. Vanghan, *Plastics*, *VIII*, 308 (1958).
9. W. B. Smith and H. E. Temple, *J. Phys. Chem.*, **72**, 4613 (1968).
10. H. H. Jellinek and G. White, *J. Polym. Sci.*, **6**, 745 (1951).
11. H. T. DeBoer, *Trans. Faraday Soc.*, **32**, 10 (1936).
12. H. Keskkula, A. E. Platt, and R. F. Boyer, *Encyclopedia of Chemical Technology*, 2nd Ed., Vol. 19, Wiley, New York, 1969.
13. E. R. Wagner and L. M. Robeson, *Rubber Chem. Technol.*, **43**, 1129 (1970).
14. G. Gooberman and J. Lamb, *J. Polym. Sci.*, **42**, 35 (1960).