

THE EFFECT OF CRYOGRINDING ON THE MOLECULAR WEIGHT OF
SAMPLES OF POLYISOBUTYLENE

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INTRODUCTION

A significant recent development in polymer technology is the discovery that megadalton-molecular-weight macromolecules can be dissolved instantaneously in liquids which are normally solvents for the materials. This finding portends increasing development and use of ultra high molecular weight macromolecules deriving from the superior effects they exhibit in a variety of applications. Past studies have demonstrated that macromolecules, added in small quantities, (1) enhance the flow of liquids through pipelines; (2) impart high extensional viscosities to and (3) impede the aerosolization of liquids in which they are dissolved. The latter is a property of antimisting fuels.

In the event that antimisting fuels gain wide use, a not inconsiderable facilitation of the feasibility might well be the on-site dissolution of the macromolecules in the fuels. This requirement is occasioned by the high susceptibility of some dissolved macromolecules to shear degradation; a concomitant of fuel transportation and transfer by pumping. The cryogenic comminution and subsequent blending of macromolecules with the fuels offers a direct route to instantaneous dissolution. The process is described elsewhere (3-5).

The antimisting effect is a strong function of the molecular weight of the additive (2, 6, 7). Consequently, an understanding of the effect of cryogrinding on the molecular weight of a potential antimisting fuel additive is required. In this study, samples of polyisobutylene of three different molecular weights were cryofractured and dissolved. Measurements of the viscosity and height-at-break in a ductless siphon (8) of the solutions were compared with those of solutions of unground samples and the comparative values were used as indicators of the extent of degradation.

EXPERIMENTAL

Samples of BASF polyisobutylene of three different molecular weights (B-100, B-200, B-200-246) were fractured in a mill, under nitrogen, at 77°K. However, they were not added immediately to the solvent as was the procedure followed in the work reported earlier. Instead, the samples were allowed to warm to room temperature under nitrogen and each was dissolved in isooctane in the usual manner, i. e., with occasional swirling in a flask over a period of several days. Simultaneously, unground samples of the same materials were similarly dissolved.

The viscosity and ductless siphon measurements were made on relatively low concentrations of the samples, because the reduced viscosities become nonlinear at concentrations near 0.1 wt % in good solvents for the molecular weights used in this study.

The data are displayed in Table I.

CONCLUSIONS

The viscosity data show that there was apparently no detectable degradation on cryogrinding the sample with the lowest molecular weight. The sample with the intermediate molecular weight suffered a molecular weight decrease of a bit above 5%. It was reported earlier that cryogrinding reduced the molecular weight of a sample of B-200 by about 6% (5). In that instance, \bar{M}_v was determined in cyclohexane at 30°C, with the material cryoground directly into the solvent and the concentration measured by weight after precipitation of the macromolecules from solution with acetone. The molecular weight of the sample with the highest molecular weight decreased by about 9%. The relative decrease in the molecular weight on cryogrinding,

$$\frac{\overline{\Delta M}_v\%}{\overline{M}_v}$$

approaches a limiting value of 1.5.

TABLE I
VISCOSITY AVERAGE MOLECULAR WEIGHT^a AND REDUCED HEIGHT-AT-BREAK OF
SOLUTIONS OF POLYISOBUTYLENE IN ISOCTANE AT 20°C

Sample	$\overline{M}_v \times 10^{-6}$ (g/mol)	$C \times 10^{-2}$ (g/dl)	h/C cm (g/dl)
B-100 (unground)	1.00	1.91	0
		3.76	0
		7.74	0
B-100 (cryoground)	1.00	3.83	0
		5.94	0
		7.72	0
B-200 (unground)	3.59	3.84	11.9
		5.70	12.9
		7.69	13.8
B-200 (cryoground)	3.40	4.03	14.2
		5.15	14.6
		8.07	16.3
B-200-246 (unground)	5.96	3.89	53.8
		5.91	54.7
		7.85	56.8
B-200-246 (cryoground)	5.42	3.85	43.7
		5.82	48.0
		7.76	49.3

a. $[\eta] = 3.06 \times 10^{-4} \overline{M}^{0.65}$ (9)

The reduced height-at-break data reveal a strong molecular weight dependency. Whereas the cryogrinding appears to have improved the viscoelastic properties of the sample with intermediate molecular weight, it causes a decided decrease in the effect in the sample with the highest molecular weight. The latter change is in the expected direction, commensurate with the degradation revealed by the viscosity measurements. In the cryogrinding process free radicals are generated (5) and while the viscosity average molecular weight decreases by about 5% for the B-200 sample, the alteration of the molecular weight distribution due to post-grinding free radical coupling might conceivably lead to an increase in the reduced ductless siphon height-at-break because in the polyisobutylene/isooctane system, the intrinsic viscosity is related to

$$\overline{M}_v^{0.65}$$

whereas the height-at-break is proportional to

$$\overline{M}_v^{2.3}$$

A relatively few such coupled molecules would contribute far less to the shear viscosity than to the extensional viscosity. Indeed, it may well be that only the very largest molecules in a sample contribute to the antimisting effect.

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