A New Method for the Quantitative Verification of the Butadiene-Styrene Copolymer

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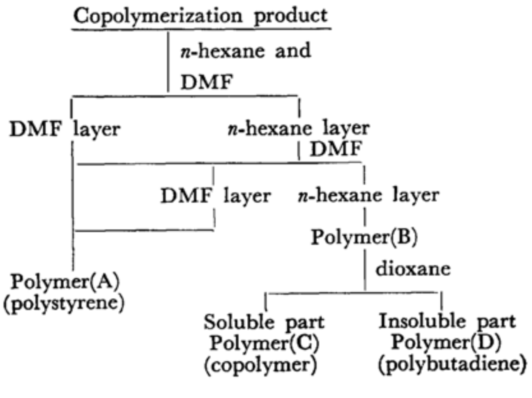
A new method to separate the homopolymer from butadiene-styrene copolymerization product, a "two-layer extraction method," has been developed.

Many new catalyst systems and copolymerization techniques (random, block or graft *etc.*) have previously been employed in the preparation of the butadiene-styrene copolymer.

It is important to characterize these products and identify the copolymer in the light of the evaluation of catalyst systems, copolymerization methods, and the physical properties of the products. Several solvent-extraction methods and fractional extraction methods have been employed in order to verify the existence of the copolymer and to separate a homopolymer from the copolymerization product. By these methods, however, a quantitative treatment was difficult. Moreover, the selection of a solvent and a nonsolvent was troublesome.

We have now succeeded in making a quantitative separation of the homopolymer from copolymerization products by a "two-layer extraction method," using *n*-hexane and *N, N*-dimethylformamide (DMF); the separation is accompanied by a dioxane extraction.

The butadiene-styrene copolymerization product (1.0 g) was dissolved or suspended in *n*-hexane (200 m*l*) under stirring for *ca.* 50 hr; then the solution or the suspension was placed in a 500 m*l* separating funnel and 100 m*l* of DMF was added. The funnel was shaken for *ca.* 15 min and then left standing for 1 hr, after which two layers, (the *n*-hexane layer(upper) and the DMF layer (lower)), were separated. The polymer (A) dissolved in the DMF layer and the polymer (B) dissolved or suspended in the *n*-hexane layer were isolated and dried under a vacuum. The polymer (B) was then further extracted with dioxane to



separate a dioxane-insoluble part (C) from a dioxane-soluble part (D).

The separation of homopolystyrene from the copolymerization product can be effectively carried out by the "two-layer extraction method" using *n*-hexane and DMF. Table 1 shows the results obtained by applying this method to a mixture of polystyrene and polybutadiene, or to each homopolymer. It is evident from the table that the homopolymers were separately extracted by the respective solvents, *i. e.,* polybutadiene by the *n*-hexane and polystyrene by the DMF.

Next, this method was applied to butadiene-styrene copolymerization product, and the copolymerization efficiency was determined by the following equation:

TABLE 1. EXTRACTION RESULTS OF HOMOPOLYMERS AND POLYBUTADIENE-POLYSTYRENE MIXTURES BY THE TWO LAYERS METHOD

No.	Polymer mixture				Polymer A		Polymer B		Recovered³⁾
	PBD¹⁾ part		PST part		DMF soluble part		*n*-Hexane part		
	wt %	$[\eta]$	wt %	$[\eta]$	wt %	St %²⁾	wt %	St %	wt %
1-1	100	3.07	—	—	0	0	97.3	0	97.3
-2	—	—	100	0.082	99.5	100	0	0	99.5
-3	75	3.20	25	0.688	24.1	100	73.0	0	97.1
-4	75	3.20	25	0.082	23.8	100	72.5	0	96.3
-5	75	1.17	25	0.688	20.6	100	75.0	0	95.6
-6	75	1.17	25	0.082	20.0	100	76.5	0	96.5
-7	75	2.08⁴⁾	25	0.082	20.2	100	72.6	0	92.8
-8	90	3.39	10	0.082	10.3	100	85.7	0	96.0

1) Cis 1, 4 polybutadiene (cis content 95.8%)

2) Styrene content was measured by IR analysis. Thus, we prepared various compositions of mixture of polystyrene and polybutadiene which had a similar microstructure to the sample to be analyzed, plotted $DCH_2(2930\ cm^{-1})/DC_6H_5(700\ cm^{-1})$ and each composition from the IR chart of each polymer mixture, and determined styrene content of each sample from this calibration curve.

3) Methanol soluble part has not been recovered.

4) Li catalyzed polybutadiene (cis content, 35.4%)

TABLE 2. EXTRACTION RESULTS OF VARIOUS TYPE OF BUTADIENE-STYRENE COPOLYMERIZATION PRODUCTS BY THE TWO LAYERS METHOD

No.	Polymerization catalyst	Copolymer type	Commercial brand	Styrene content %
2-1	Radical type (emulsion)	random	SBR 1502 (JSR)	25.3
-2	Li type (solution)	random	Duradene (Firestone)	24.2
-3	Li type (solution)	random	Solprene 1204 (Phillips)	25.0
-4	Li type (solution)	block	Solprene 1205 (Phillips)	28.7
-5	$Co(acac)_2$-$Al_2Et_3Cl_3$*1	random	—	9.3
-6	$TiCl_4$-$AlEt_3$*1	random	—	28.4

No.	Polymer A DMF soluble part wt %	Polymer B *n*-hexane part St %	Recovered*2 %	Copolymerization efficiency %
2-1	trace	25.3	91.80	≒100
-2	trace	24.0	97.30	≒100
-3	trace	25.0	96.17	≒100
-4	0.13	28.7	95.28	≒100
-5	4.0	5.9	94.60	57.0
-6	24.28	5.8	95.50	14.5

*1 Copolymerization was conducted at 40°C.

*2 Methanol soluble part has not been recovered.

TABLE 3. EXTRACTION RESULTS OF POLYBUTADIENE-BUTADIENE-STYRENE COPOLYMER MIXTURE BY THE DIOXANE METHOD

No.	Polymer	Styrene content %	Polymer C Dioxane soluble part		Polymer D Dioxane insoluble part	
			wt %	St %	wt %	St %
3-1	SBR 1502 (JSR)	24.5	100	24.5	—	—
-2	Polybutadiene-copolymer*[1] mixture (5 : 5)	8.7	51.0	11.7	49.0	1.8
-3	Copolymer*[1]	14.4	100	14.4	—	—

Extraction condition

Polymer: 1.0 g; Solvent: dioxane 30 m*l*; Extraction time: 50 hr at 25°C.

*[1] Copolymer obtained by $Ni(acac)_2$-BF_3Et_2O-$AlEt_3$ catalyst system (Japanese Pat. 42-7795) was used after two layers extraction method.

Copolymerization efficiency(%)=

$$\frac{S_T-S_H}{S_T}\times 100=\frac{S_C}{S_T}\times 100$$

S_T: total styrene content (%)
S_H: homopolystyrene content (%)
S_C: copolymerized styrene content (%)

The results obtained are shown in Table 2.

We also found that dioxane extraction after the removal of homopolystyrene could be used to separate polybutadiene from a copolymer-polybutadiene mixture. Some results of the dioxane extraction are shown in Table 3.

The "two-layer extraction method" is also effective for a liquid-liquid extraction. This method is especially recommended for the isolation of a graft copolymer from the reaction products. The method described above was also applied to an isoprene-styrene copolymerization product. Similar quantitative extraction results were obtained. This method may also be applied to other conjugated diolefin-vinyl compound copolymerization products, such as butadiene-acrylonitrile, butadiene-methylmethacrylate, and isoprene-methylmethacrylate.