Block and Graft Copolymers of Pivalolactone. 3. Grafts on Ethylene Copolymers

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ABSTRACT: The anionic ring-opening polymerization of pivalolactone (2,2-dimethylpropiolactone, PVL) was used to graft side chains on poly(ethylene-*co*-vinyl acetate-*co*-methacrylic acid) and similar copolymers. Grafting was effected in homogeneous solution in tetrahydrofuran using the tetraalkylammonium salts for initiation. Graft frequency was determined by the concentration of copolymerized methacrylic acid and average graft degree of polymerization calculated from the mole ratio of PVL to carboxyl sites. Forming highly crystalline microdomains as they increased in length, the polypivalolactone side chains increased minimum flow temperatures, limited solubility, enhanced spherulite formation, and reinforced the mechanical properties of the base resin.

I. Introduction

Unique suitability of pivalolactone as a grafting monomer was reported briefly in two communications[1,2] and details of the property changes observed are now being added to the literature.[3-6]

Ethylene copolymers can exhibit a range of crystallinity, solubility, and softening behavior depending on stereoregularity and composition. The effect of grafting pivalolactone on such properties was studied with the business objective of extending their use temperature range and with the fundamental objective of exploring the influence of its high polymer crystallinity on compositions ranging from elastomeric to plastic.

II. Experimental Section

The pivalolactone (2,2-dimethylpropiolactone, PVL) was 99.9+% pure by gas chromatography, stored in a freezer at −25 °C (248 K) as a crystalline solid, and filtered through neutral alumina just before use to remove traces of homopolymer sometimes observed after long storage.

The monomer is a colorless liquid at room temperature with a sharp, somewhat lachrymatory odor that encourages its handling in the hood. It was prepared by the dehydrohalogenation of chloropivalic acid.[7] Its properties and polymerization have been reviewed by Mayne.[8]

Unpublished work at Haskell Laboratory, E. I. du Pont de Nemours and Company, has shown that PVL caused skin tumors in mice when applied as a 25% solution in acetone five times a week for most of the life span of the mice. The time for tumor formation was greater than that for β-propiolactone, applied at 5% concentration as a positive control in the test, and the extent of tumor formation was much less.

The backbone copolymers were commercial and experimental grades of ethylene copolymers. The poly(ethylene-*co*-vinyl acetate-*co*-methacrylic acid) materials used for the comparisons presented in this paper were grades of Du Pont Elvax resins. Content of copolymerized methacrylic acid was determined by titration.

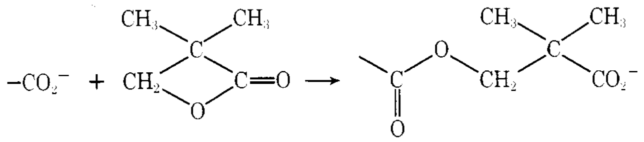
In a typical procedure 0.2 kg of the backbone resin was dissolved in 600 mL of tetrahydrofuran, the solution was warmed to gentle reflux (75–85 °C, 348–358 K), and 20–50% of the carboxyl groups in the base resin were neutralized with tetrabutylammonium hydroxide (1 M in methanol). The pivalolactone was then added to the well-stirred system as rapidly as the exotherm (or experimental limitations) would permit, and heating and stirring continued for 30–120 min more to complete the reaction. When the system remained fluid it was acidified with concentrated hydrochloric acid before precipitating the product in warm water in a blender. The resulting solid was washed well with water and dried in a vacuum oven at 80 °C (353 K). Recovery of the added pivalolactone as grafted polymer was normally above 95%, often complete.

Automated minimum flow temperatures (AMFT) were determined in a melt indexer with an orifice of 0.21 cm at a loading of 3 kg/cm^2 and the temperature was programmed to increase at 1 °C/min.

The polymers were compression molded between aluminum sheets into 10 × 10 × 0.13 cm blanks. Microtensile specimens with cross-sectional area in the tested region of about 0.06–0.07 cm^2 were cut from these sheets and tested after conditioning at 23 °C (295 K) and 50% relative humidity. Pressing cycles included 120 s preheat at flow temperatures, 120 s at full pressure (700 kg/cm^2), and cooling under pressure.

III. Results and Discussion

A. Grafting Variables and Interpretation. These graft polymerizations were conducted in homogeneous solution at moderate temperatures to optimize conditions for the simple ring-opening polymerization. This anionic polymerization, propagated by the carboxylate anion, is a "living" system since the anion is quite stable, chain transfer to monomer does not occur, and chain termination reactions are normally absent.[8] As a further consequence of the anionic mechanism and the similarity of initiating and propagating rates, molecular weight distribution of the grafted side chains was expected to be narrow.



(1)

Solvents for these ethylene copolymer backbones were easily chosen and for this grafting reaction are preferably polar and aprotic. Tetrahydrofuran offers fast initiation, high propagation rates, and easy isolation of the products by precipitation in water. Reactions in toluene were slower, but the thermal and mechanical properties of products isolated by precipitation in ethanol were very similar to those of products prepared in tetrahydrofuran.

Almost any carboxylate is an effective initiator.[9] The cation, however, should not coordinate strongly with or interfere with the reaction of the carboxylate. Tetraalkylammonium ions were especially effective, with no evidence of any advantage from tetramethyl to tetrabutyl. In less polar solvents the tetrabutylammonium cation may be preferred. Tetrahydroxyethylammonium cations were not useful, and it should be noted that hydrogen bonding of alcohols or phenols to the carboxylate could provide interference. However, small amounts of methanol and water, as present in undried solvents or as added in neutralization, had no detectable influence on completion of reaction or product properties.

Inorganic counterions such as sodium, calcium and lithium were not successful, although some evidence for grafting was observed when lithium ion was complexed with tetramethylethylenediamine and hexamethylphosphoramide. Products were lower in graft degree of polymerization than those obtained with quaternary ammonium cations.

The effects of a grafted monomer on the properties of the

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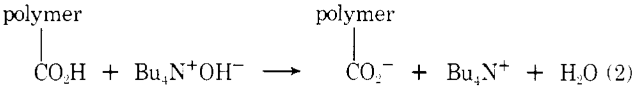
backbone structure are determined by graft frequency and side chain length. In the next few paragraphs our assumptions and calculation of these two parameters are explained.

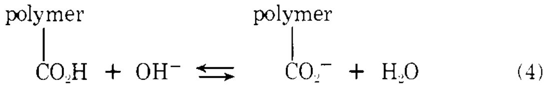
In the ethylene copolymers used in this work, copolymerized methacrylic acid provided the grafting sites, converted to active initiation by reaction with tetrabutylammonium hydroxide.


$$\underset{\text{CO}_2\text{H}}{\overset{\text{polymer}}{|}} + \text{Bu}_4\text{N}^+\text{OH}^- \longrightarrow \underset{\text{CO}_2^-}{\overset{\text{polymer}}{|}} + \text{Bu}_4\text{N}^+ + \text{H}_2\text{O} \quad (2)$$

Complete neutralization of the carboxyl groups was unnecessary since all carboxyls can participate in initiation through proton exchange, a relatively rapid reaction.

$$\text{R-CO}_2^- + \text{R}'\text{-CO}_2\text{H} \leftrightharpoons \text{R-CO}_2\text{H} + \text{R}'\text{-CO}_2^- \quad (3)$$

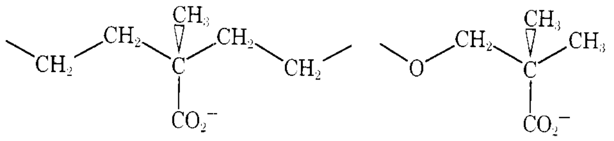
Neutralization levels from 2 to 100% were explored in graft preparations; comparisons in a following section (Tables I and II) verified the assumption of reaction 3. Consequently neutralization levels of 20–35% were normally employed to take advantage of the effect of the following equilibrium in depressing the already low concentrations of hydroxyl or methoxyl anions, potential initiators of homopolypivalolactone.


$$\underset{\text{CO}_2\text{H}}{\overset{\text{polymer}}{|}} + \text{OH}^- \rightleftarrows \underset{\text{CO}_2^-}{\overset{\text{polymer}}{|}} + \text{H}_2\text{O} \quad (4)$$

Hall[9] compared initiation rates of different carboxylates and demonstrated that the propagation rates were independent of the initiating species. In tetrahydrofuran propagation was as fast as initiation.

Yamashita and Hane[10] attributed unreacted polystyrene carboxylate initiator to nucleophilicity less than that of the propagating carboxylate, but sodium counterions may have prevented effective initiation.

In this work, the similarity in the structure of the initiating carboxylate site and the propagating site should lead to quite similar initiating and propagating rates.



The precautions taken in establishing the carboxylate anion as the initiating site, the depression of HO^- and CH_3O^- concentrations, and the absence of chain transfer to monomer[8] support the assumption that grafting efficiencies were high. The extractibility of the grafted products denied the presence of high molecular weight homopolymer (see further), but definitive extraction of homopolypivalolactone from these substrates was not obtained.

In light of the above considerations, graft frequency was calculated directly from the concentration of carboxyl groups in the backbone polymer as determined by analysis. Backbone molecular weight per site was calculated as the neutralization equivalent.

Since conversions of monomer to grafted polymer were normally as close to quantitative as our laboratory operations would permit, we calculated the number average graft degree of polymerization as the mole ratio of pivalolactone to the initiating carboxyl sites.

Validity of these calculations is supported by the "living" anionic mechanism of graft formation which develops a narrow Poisson graft molecular weight distribution. It should be noted that departure from such ideal distribution is invited by partial neutralization of carboxyl function, especially as the time of reaction (availability of monomer) becomes short. However, in related work Thamm et al.[8] prepared homopolypivalolactone, under similar conditions, using 50% neutralization, to a degree of polymerization of 22 with a polydispersity index ($\overline{M}_w/\overline{M}_n$) of 0.99 (experimentally indistinguishable from the theoretical value of 1.05).

Table I
Effect of Partial Neutralization on Polymer Properties

	Backbone[a] polymer	Graft copolymers[b]		
% neutralization		20	20	60
% pivalolactone		23	23	24.5
Graft DP		26	26	28.5
Min. flow temp, K	394	465	467	465
Yield stress, MPa	4.77	7.10	7.31	8.51
Yield elongation, %	92	20	24	21
Elongation at break, %	930	670	660	665
Modulus to 100% elongation, MPa		7.99	8.13	9.58

[a] 20% vinyl acetate, 1% methacrylic acid; 8000 molecular weight per carboxyl site; $\overline{M}_w$ = 96 000. [b] $Bu_4N^+OH^-$ used as base.

Table II
Effect of Partial Neutralization on Polymer Properties

	Backbone[a] polymer	Graft copolymers[b]			
% neutralization		2	4	20	60
Min. flow temp, K	263	344	342	358	351
Yield stress, MPa	3.0	5.2	5.6	5.4	5.2
Yield elongation, %	60	26	30	39	27

[a] 25% vinyl acetate, 1% methacrylic acid; 8700 molecular weight per carboxyl site; $\overline{M}_w$ = 65 000. [b] Containing 16.5% pivalolactone, with $Et_4N^+OH^-$ as the base.

B. Effects of Grafting. Under these conditions grafting with pivalolactone leads to the growth of polyester side chains with a strong tendency to crystallize from the ethylene copolymer substrate. The presence of microdomains of crystalline polypivalolactone has been demonstrated in other substrates with wide-angle x-ray and electron microscopy.[4]

Differential scanning calorimetry curves show the endotherm marking the melting temperature of the polypivalolactone side chains distinct from those of the copolymer substrate (Figure 1). The exotherm on cooling is also well defined.

To the extent that these side chains form crystalline microdomains of polypivalolactone, they develop a thermoplastic network within the backbone substrate. For example, the polymer whose DSC curve is shown in Figure 1 flows only when the temperature of the poly(PVL) endotherm is reached and the crystalline regions melt.

Since the melting temperatures of these polypivalolactone side chains increase with their degree of polymerization, minimum flow temperatures were correlated with their length. The effect is illustrated with three different substrate compositions in Figure 2. Homopolypivalolactone segments of corresponding degrees of polymerization show a melting point curve 5–10 °C higher. Similar curves were obtained with a variety of ethylene copolymers containing 0 to 35% vinyl acetate and 17 to 38% isobutyl acrylate.

Melt viscosities above the melting point of the side chains were somewhat lower than that of the substrate copolymer for the example illustrated in Figure 3. An increase in melt viscosity was observed with pivalolactone grafting on EPDM substrates of much higher molecular weight.[6] (EPDM, an acronym for poly(ethylene-*co*-propylene-*co*-1,4-hexadiene), e.g., NORDEL, Du Pont's hydrocarbon elastomer.)

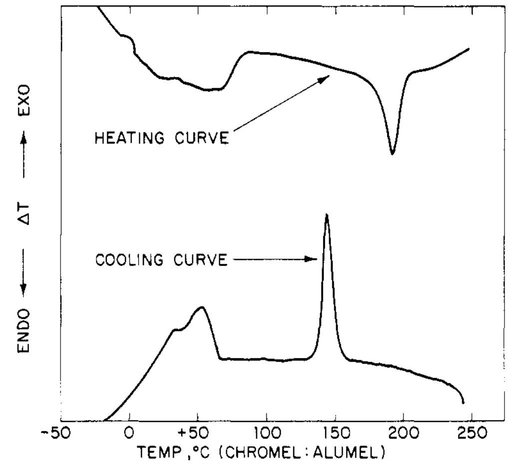


Figure 1. Differential scanning calorimetry curves of poly(ethylene-*co*-vinyl acetate-*co*-methacrylic acid-*g*-pivalolactone). Base resin composition E7 3.5%, VOAc 25%, MAA 1.5%; $\overline{M}_w$ = 13 000; PVL grafted; 18%, DP 12.

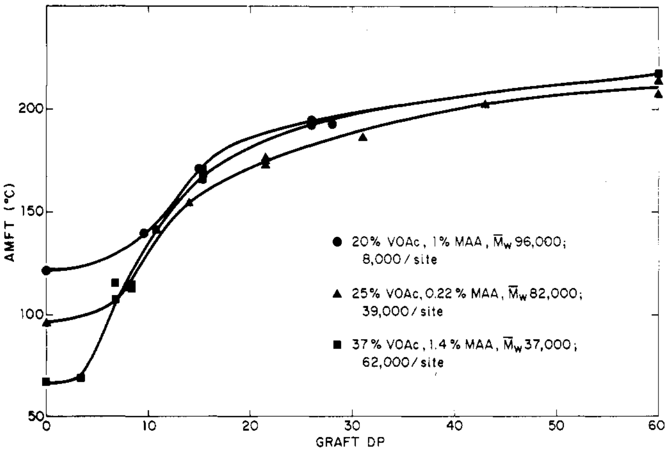


Figure 2. Effect of graft length on automated minimum flow temperatures.

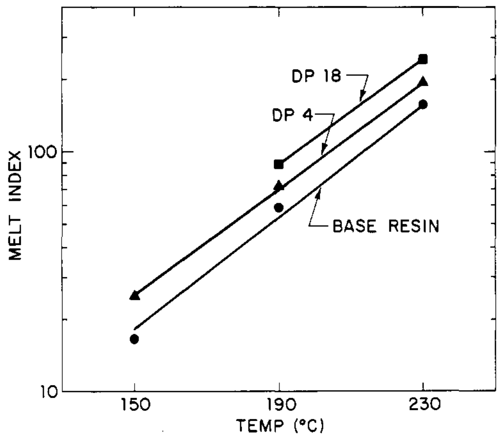


Figure 3. Effect of grafting on melt index. Base resin E 59.6%, VOAc 38.8%, MAA 1.6%; $\overline{M}_w$ = 33 000.

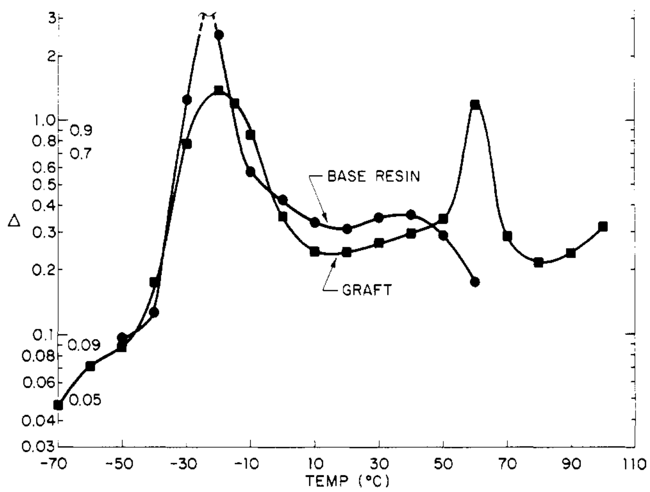


Figure 4. Loss curve from torsion modulus data. Base resin E 61.3%, VOAc 37.3%, MAA 1.4%; $\overline{M}_w$ = 37 000; graft 10% PVL, for a DP of 7.

Torsion modulus loss curves (Figure 4) reveal some evidence for the glass transition of polypivalolactone, reported[11] to be −10 °C (263 K). The melting transition for the ethylene copolymer (60 °C, 333 K) is observable because of the structural support of the grafted side chain domains.

The curves in Figure 5 illustrate the sensitivity of creep resistance to side chain length and melting behavior.

The mechanical effects of pivalolactone side chains are readily seen in the breaking properties shown in Figure 6. The curves show the softening effect at short chain lengths (less than 5 wt % PVL), and the onset of reinforcement and decrease in elongation at break as side chain lengths exceed 3.5–4 and a separate phase begins to develop. The effects so readily seen in this soft copolymer are less pronounced at much higher substrate molecular weights and lower vinyl acetate contents.

The modulus of these grafted copolymers responds to side chain length just as minimum flow temperatures do. The divergence of the curves in Figure 7 is attributable to such differences. The lower curve joins data for compositions with side chain lengths of 1.4 to 6 units and shows the softening action of very short chains in this substrate. Side chain lengths in the middle two curves range from 5 to 19, and the least frequently grafted series of compositions had side chain lengths of 22 to 78 units.

This sensitivity of modulus to side chain length seems most readily understood in terms of the increasing ease of phase separation and crystallization as DP increases. These effects recall to mind the observations of Kraus et al.[12] that the viscoelastic properties of butadiene–styrene block copolymers were essentially determined by the terminal blocks, a result best rationalized in terms of a two phase domain structure persisting to a significant degree into the melt.

The sensitivity of flow temperatures and moduli to graft length enabled us to verify the assumption that all carboxyl groups were involved as grafting sites. The date in Tables I and II compare the products obtained in grafts on two copolymer substrates using different levels of neutralization. The similarity of the products obtained could not result if an equilibrium among all carboxyls present did not exist.

During the grafting reaction, solution viscosity increases and may culminate at higher graft modifications in gelation of the system. Since polypivalolactone is insoluble in common organic solvents, solubility of the grafted products is rapidly lost as side chain length increases.

Extractibility of a variety of compositions, prepared from a variety of ethylene–vinyl acetate copolymers, was determined by a 5-h Soxhlet extraction with toluene (Figure 8). Solution was complete up to a side chain DP of about 25 (indicating the absence of detectable amounts of high molecular weight homopolymer) but decreased rapidly at higher side chain lengths. In substantial corroboration, homopolypivalolactone of a DP of 10 was completely dissolved in hot toluene, while a sample with a DP of 20 was less than 15% dissolved. With tetrahydrofuran as solvent, the limiting graft DP was seven; with the even poorer solvent cyclohexane, the limiting

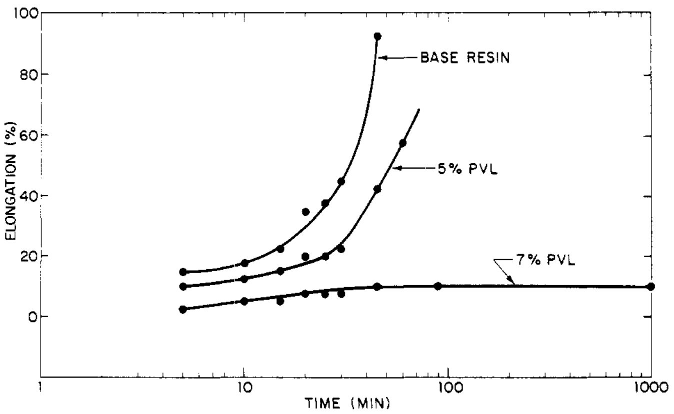


Figure 5. Tensile creep at 343 K and 47 kPa stress. Base resin composition E 71%, VOAc 28%, MAA 1%; $\overline{M}_w$ = 63 000.

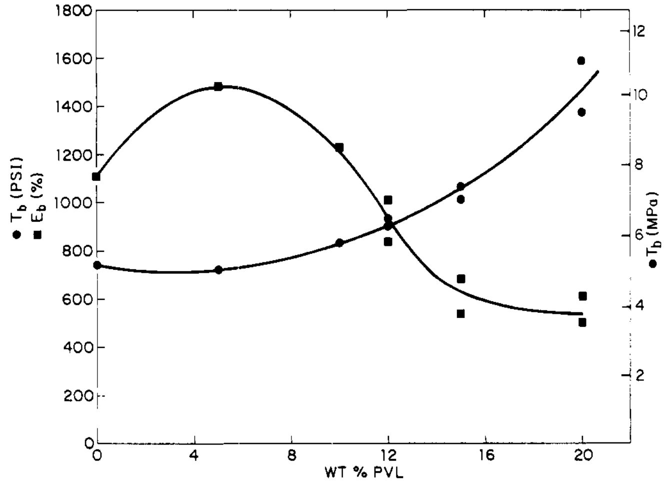


Figure 6. Effect of grafted pivalolactone on tensile strength (T_b) and elongation at break (E_b). Base resin E 61.3%, VOAc 37.3%, MAA 1.4%; $\overline{M}_w$ = 37 000.

graft DP was 2.5. Residual extractibility at high side chain lengths is attributed to the presence of substrate molecules without grafting sites, since methacrylic acid contents were very low.

Spherulitic structure has been observed in block polyether–urethanes[13] and polyether–esters.[14] In such the smaller crystalline domains of main chain hard segments are involved in spherulite formation. Since polypivalolactone readily forms large spherulites when crystallized from the melt, these graft copolymers were examined for spherulite formation. Samples, melted on a microscope slide and pressed thin with a coverglass, were cooled slowly over 60–90 min and examined at 6-25X magnification under cross polaroids.

The ethylene-vinyl acetate substrates used here exhibited very small spherulites, to some degree dependent on ethylene content. Spherulite size was strongly increased by grafting as little as 6–10% pivalolactone. The spherulitic structure in such minor modifications necessarily involved primarily polyethylene order, and some samples clearly exhibited incipient order or orientation that had not culminated in spherulite formation. It would seem that microdomains of polypivalolactone grafts were effectively nucleating order in the backbone substrate.

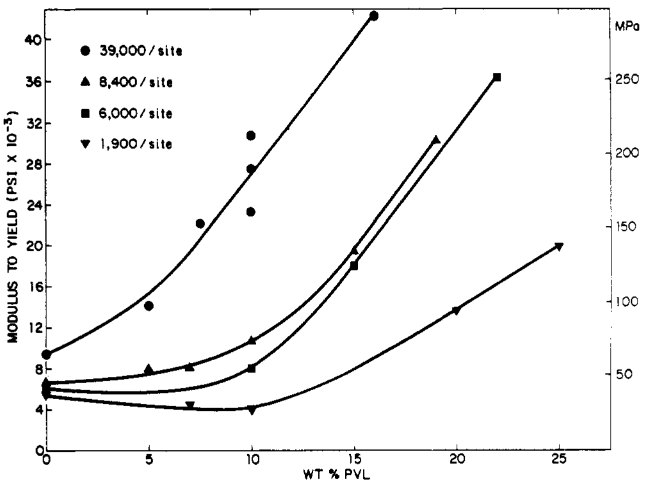


Figure 7. Effect of graft frequency and length on modulus (substrate; poly(ethylene-*co*-vinyl acetate-*co*-methacrylic acid)).

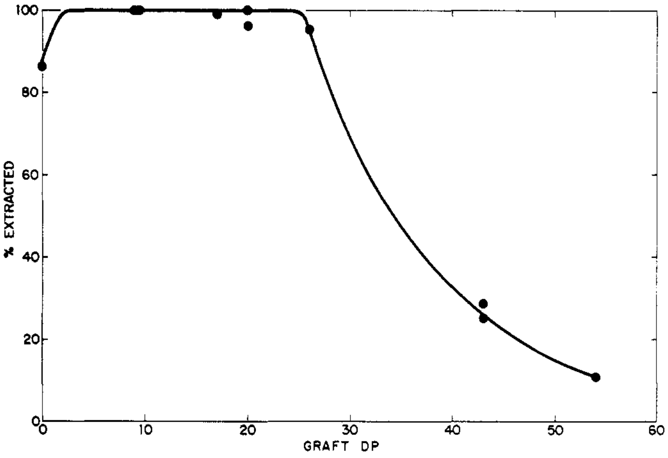


Figure 8. Soxhlet extractions with toluene (substrate; poly(ethylene-*co*-vinyl acetate-*co*-methacrylic acid), of variable composition).

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