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Graft and crosslinked copolymers by nucleophilic reaction between maleic anhydride copolymers and carbanions

II. Synthesis and characterization of copolymers with middle-low grafting degree and long lateral chains

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SUMMARY

Grafting of polystyryl and copoly(styrene-b-isopren)yl macrocarbanions onto ethylene-maleic anhydride alternating copolymer was carried out under reaction conditions such as to obtain copolymers with middle-low grafting degree and long lateral chains. In order to ascertain the absence of secondary reactions, the coupling of n-BuLi with succinic anhydride was investigated, and no secondary reaction was observed. The graft copolymers, wich have molecular weights and elemental composition in good agreement with those expected, were studied by IR spectroscopy and DSC. Both spectra and calorimetric curves confirm the structures assigned to the copolymers. The tensile properties of the copolymers with copoly(styrene-b-isoprene) lateral chains were also investigated. The properties appear very dependent on the degree of grafting, on the solvent (benzene or THF) from which the specimens were deposited, and on their thermal history.

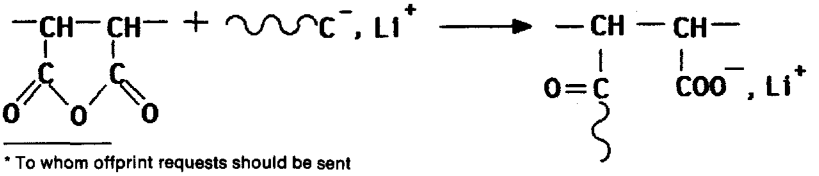
INTRODUCTION

It is well known that a characteristic feature of anionic polymerization in homogeneous phase is the lack of termination reactions. Polymers obtained by this method have carbanionic end groups which can undergo coupling reactions by displacing heteroatoms in functional reagents, such as alkyl halides, oxiranes, esters (1-3).

By adding a solution of living polymeric carbanions to a solution of a polymer which can act as a polyfunctional reagent, a grafting reaction occurs. In previous papers we have described the preparation and some properties of graft copolymers obtained by coupling living anionic polystyryl- and polyisoprenyl-lithium onto alternating maleic anhydride-ethylene and maleic anhydride-styrene copolymers (4-7). Some of these copolymers have been tested for haemocompatibility in view of a possible use of them as biomaterials (6).

The present investigation concerns the preparation and characterization of graft copolymers in which the backbone is an alternate ethylene-maleic anhydride copolymer and the grafts are both polystyrenes and diblock copolymers poly(styrene-b-isoprene).

To obtain graft copolymers of satisfactory homogeneity in composition, the nucleophilic attack of carbanionic species on the anhydridic groups should generate only one graft, i.e.:



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Since polystyryllithium reacts with gaseous carbon dioxide to give 60% polystyrenecarboxylic acid, 28% dipolystyrylketone and 12% branched tripolystyrylcarbinol (8), and with ketones to give tertiary alcohols (9), the possibility that more than one carbanionic chain may react with the same anhydridic group cannot be excluded a priori. In order to check this possibility, we have studied the reaction between n-butyllithium and succinic anhydride as model molecules.

EXPERIMENTAL

Materials

Styrene (Carlo Erba RPE) and isoprene (Fluka AG Buch SG) were purified as previously described (10), and distilled under vacuum from n-BuLi just before use.

Succinic anhydride (SA, Carlo Erba RPE) was purified by vacuum sublimation.

Alternating ethylene-maleic anhydride copolymer (EMA, Aldrich Chem. Co.) was purified as described in Part I (4), and dried in vacuum oven at 150°C for three days. Its 1:1 composition was confirmed by titrating the acidic groups by means of a METROHM pHmeter. The EMA solution in THF was prepared and stored on vacuum line. The absence of active H atoms in the copolymer was tested by reaction with n-Buli in the gas evolution measuring apparatus already described (5).

Ciclohexane (CH, Carlo Erba RPE) was conventionally purified, collected onto molecular sieves in the vacuum line and distilled from nBuLi just before the use.

Tetrahydrofuran (THF, Aldrich gold label), after conventional purification, was stored in the vacuum line over sodium naphthalene from which it was distilled before the use.

n-BuLi and sec-BuLi (EGA CHEMIE) were 1.6 M solutions in n-hexane, which were diluted and collected into fragile bulbs prepared with the middle point method (10,11). Before the use, the actual concentrations of both reagents were determined by Gilman's method (12).

Coupling of n-BuLi with SA

The reactions were carried out under vacuum at 0°C by adding a 1.6M n-BuLi solution in n-hexane to a dilute THF solution of SA under stirring. THF was kept in large excess owing to the low solubility of SA in hydrocarbon solvents. A pale grey solid was formed all through the reaction. The reaction mixture was allowed to stand two hours at room temperature under efficient stirring; after opening the apparatus, the solid was separated, washed with Et_2O, vacuum dried and analyzed.

Grafting of macrocarbanions onto EMA

Monofunctional polystyryllithium was synthesized in THF solution; monofunctional poly(styrene-b-isoprenyl)lithium was synthesized in CH solution in order to obtain polyisoprene chains with prevalent 1-4 cis configuration. In both cases sec-BuLi was used as the initiator. Samples were withdrawn for molecular weights and yields determinations.

Just before the grafting reaction, CH was replaced by THF, owing to the EMA insolubility in this solvent. Polymerization and grafting apparatus was previously described (7). The THF solution of polymeric carbanions were added dropwise at 0°C to a THF solution of EMA (5% in weight) under stirring. The disappearance of the typical orange colour of carbanionic species in THF is almost istantaneous. The temperature was allowed to rise to 30°C and kept constant overnight.

Graft copolymers were recovered by precipitation in methanol in which they were kept under stirring for 15 hours in order to extract the eventually unreacted EMA. Afterwards, they were extracted in Soxhlet with the selective solvents methylethylketone and CH.

RESULTS AND DISCUSSION

Coupling of n-BuLi with SA as model molecules

The coupling between the model compounds, when occurring in the absence of secondary reactions, must give only lithium 4-oxo-octanoate $CH_3(CH_2)_3CO(CH_2)_2COO^- Li^+$ in nearly 100% yield. Some experimental data, obtained at different SA/n-BuLi ratios, are collected in Table 1.

Table 1
Coupling of n-BuLi with SA

Exp No	n-BuLi mol x 10^2	SA mol x 10^2	SA/n-BuLi	Product gr	Yield %
1	1.05	3.64	3.46	1.68	97.56
2	1.55	2.86	1.84	2.35	92.51
3	2.64	2.64	1.00	4.28	98.39
4	10.22	10.00	0.978	15.95	95.15

Elemental analysis of samples from Exps 1 and 3 gave the following per cent compositions:

Exp	C	H	O	Li
1	58.75	7.31	29.55	4.35
3	58.94	7.78	29.20	4.12
Calcd.	58.55	7.98	29.24	4.23

The substance obtained by acidification of the lithium salt and subsequent vacuum distillation shows physical properties in good agreement with those reported for 4-oxo-octanoic acid (13):

	Found	Reported
Boiling point,°C	170-72 (20 Torr)	156-57 (10 Torr)
Fusion point,°C	54.5	54-54.5
Fusion point of p-nitrophenylhydrazone,°C	153	152

H-NMR spectrum shows: δ = 2.6 (m,2H,CH_2COO), 2.2-1.4 (m,4H,CH_2CO), 1.2 (m,4H,CH_2) and 0.9 ppm (t,3H,CH_3).

The results confirm that SA, reacting with n-BuLi in aequimolar ratio or in excess, forms almost exclusively the γ-ketoacid expected.

Grafting of macrocarbanions onto EMA

The grafting reaction takes place as expected, with negligible termination. Number and spacing of the side chains on the backbone are regulated by the carbanions to anhydridic groups molar ratio, which has been kept low. Thus, the degree of grafting, i.e. the percentage of anhydridic functions which have reacted, does not exceed 10%. Nevertheless, owing to the high polymerization degree of the lateral chains, copolymers of high styrene and isoprene content and of high molecular weight have been obtained. Some data are shown in Table 2.

Table 2
Grafting of macrocarbanions onto EMA[a]

Exp No	Side chains kind[b]	$\bar{M}_n$[c]	$\bar{M}_n$ graft copolym. theor.	obs.[c]	Average number of grafts per molec.	EMA % in copolymers
1	St	27000	56500	55000	1.52	26.60
2	St	27000	66700	64000	1.89	22.60
3	SI	86500	1108300	986000	12.80	1.65
4	SI	86500	384300	368000	4.27	4.20
5	SI	57800	137500	135000	2.38	10.23
6	SI	57800	114400	116000	1.98	12.03
7	SI	86500	137800	136000	1.42	11.59

a) $\bar{M}_n = 15000$

b) St = polystyrene; SI = poly(styrene-b-isoprene).

c) Determined by a Knauer membrane osmometer at 30°C in THF solution.

Theoretical molecular weights, easily evaluable from the carbanions to anhydridic groups molar ratio by the relationship:

$$\frac{\bar{M}n(EMA)}{FW(EMA)} \cdot \frac{\text{moles carbanions}}{\text{moles EMA}} \cdot \bar{M}_n(\text{macrocarbanion}) + \bar{M}_n(EMA)$$

are in good agreement with those measured. These results confirm that the system is living and that no secondary reaction occurs appreciably.

Elemental analysis of samples, in which the grafts are polystyrene and the anhydridic groups are completely hydrolyzed by refluxing in THF with 0.1 N HCl, gives the following per cent compositions:

Exp		C	H	O
1	Calcd.	80.03	7.07	13.00
	Found	79.31	6.87	13.82
2	Calcd.	81.57	7.24	11.19
	Found	81.02	7.05	11.93

The IR spectra of the copolymer from Exp 1 in Table 2, performed on completely hydrolyzed samples, show absorption bands ascribable both to a poly(carboxylic acid) and to polystyrene (Figure 1). The first ones are: the broad O-H stretching absorption around 3000 cm^{-1}; the C=O stretching band at 1720 cm^{-1}; the broad C-O stretching band around 1250 cm^{-1}, partially overlapped with the polystyrene band at 1180 cm^{-1}. The second ones are: the aromatic C-H stretching peaks between 3100 and 3000 cm^{-1}, partially overlapped with the broad band of the backbone in the same region; the absorption peak at 1601.4 cm^{-1}, involving carbon to carbon stretching within the ring; the aromatic C-H out-of-plane bending peaks at 906.7 and 686.8 cm^{-1}. Other bands appear overlapped. The disappearing of the anhydridic C=O stretching bands of the substrate (1841.7 and 1768.3 cm^{-1}; overtone at 950.5 and 913.8 cm^{-1}) is due to the hydrolysis of the anhydridic groups in the copolymer.

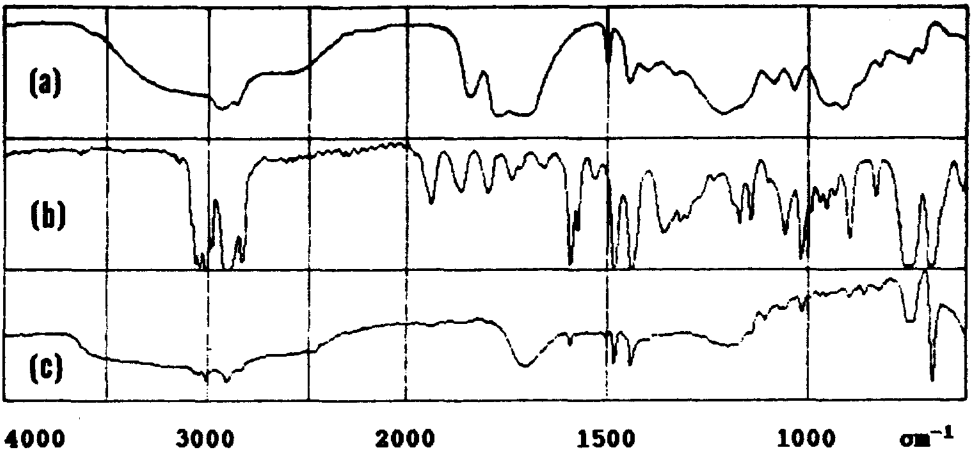

Figure 1. IR spectra of (a) partially hydrolyzed EMA, (b) polystyrene, and (c) copoly(EMA-g-styrene), (Exp No 1, Table 2), after complete acid hydrolysis in THF. Spectra performed on autosupported films.

Solubility of the graft copolymers

The graft copolymers are soluble in benzene, a nonsolvent for EMA, also when all the anhydridic groups are in hydrolized form. They are insoluble in water, acetone and methanol, in which the backbone is readily soluble.

This behaviour is quite unexpected, at least for the materials in which the EMA percentage is greater than 20% and the hydrophilic anhydridic or carboxylic groups are in large excess in comparison with the hydrophobic grafts. Likely, the molecular weights of the grafts, far higher than that of the backbone in all the materials synthesized, could play an important role on the solubility: i.e. the length of the grafts appears to overcome the low degree of grafting and the solubility to be governed by the nature of the grafts.

Thermal behaviour of the graft copolymers

Thermal analysis was performed by differential scanning calorimetry (DSC), using DSC2 Perkin-Elmer apparatus. Figure 2 shows two distinct glass transitions at about 290 K and 370 K in copoly(EMA-g-styrene), while a third glass transition appears at about 220 K in copoly[EMA-g-(styrene-b-isoprene)]. These results indicate a phase segregation in the copolymers, since the observed glass transition temperatures correspond to those of EMA, polystyrene and polyisoprene. The T_g of EMA appears unaffected by the rigid polystyrene grafts, at least at low grafting degrees; on the contrary it appears shifted towards lower temperatures when a polyisoprene sequence is inserted between the rigid backbone and a polystyrene block.

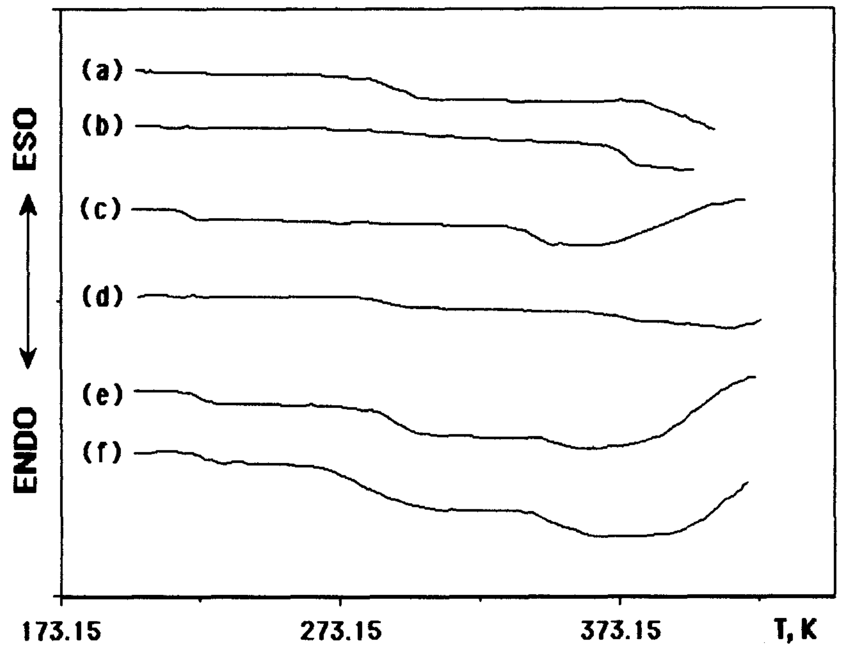

Figure 2. DSC scans of (a) EMA, (b) polystyrene, (c) poly(styrene-b-isoprene), (d) copoly(EMA-g-styrene) with average 1.52 grafts per EMA molecule, and copoly[EMA-g-(styrene-b-isoprene)], with average (e) 12.8 and (f) 4.27 grafts per EMA molecule.

Mechanical properties of the graft copolymers

Films of copoly[EMA-g-(styrene-b-isoprene)] with completely hydrolyzed anhydridic groups (EMA-g-SI) and of poly(styrene-b-isoprene) (SI) were deposited from dilute solutions in benzene and THF at 30°C on glass surfaces, from which they were removed by ultrasounds, after drying in vacuo at room temperature. The specimens, which were (1x10) cm^2 area and 200-300 μ average thickness, were tested by an Instron apparatus.

In Figure 3 they are shown stress-strain curves of SI (**a**), and of EMA-g-SI (**b**-**g**) with different grafting degrees and comonomer compositions. It appears that mechanical properties are influenced by the grafting degree, by the solvent from which the films have been deposited, and by their thermal history.

The comparison of the curves (**b**) and (**c**) indicates very different behaviours, although polyisoprene is the prevailing constituent in both copolymers. **b** is a brittle material with an ultimate tensile stress and an ultimate deformation quite low; on the contrary **c** is characterized by an higher ultimate deformation. The behaviour of copolymer **c** is quite similar to those of copolymer **g** and of the diblock copolymer **a**. These results indicate that the grafting degree influences markedly the mechanical properties: however the behaviour appears to change when the grafts per EMA molecule are still few (about four).

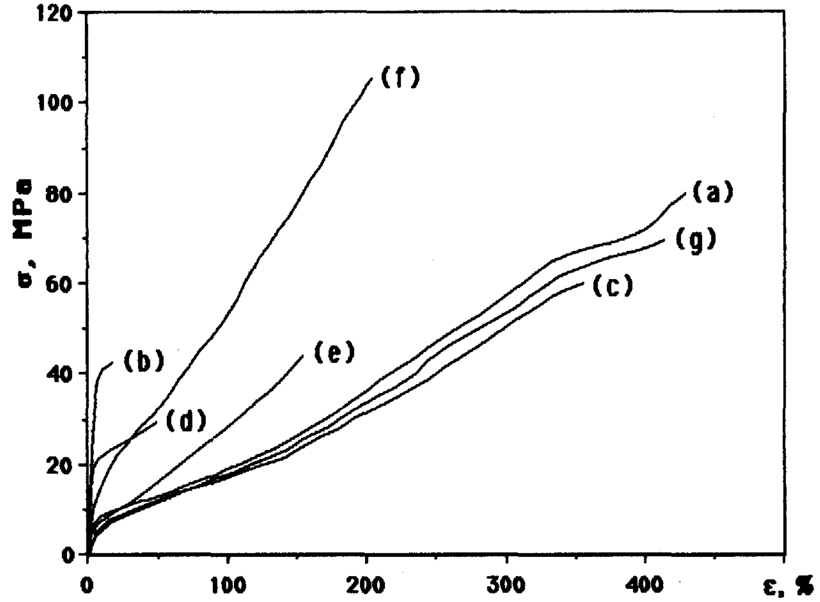

Figure 3. Stress-strain curves of: (**a**) poly(styrene-b-isoprene) and (**b**–**g**) copoly[EMA-g-(styrene-b-isoprene)], with average numbers of grafts per EMA molecule (G), and percentages of styrene (S%) and isoprene (I%): (**b**) G 1.98, S% 17.7, I% 70.0, cast from benzene; (**c**) G 4.27, S% 19.0, I% 76.5, cast from benzene; (**d**) G 4.27, S% 19.0, I% 76.5, cast from THF; (**e**) G 4.27, S% 19.0, I% 76.5, cast from benzene and annealed; (**f**) G 4.27, S% 19.0, I% 76.5, cast from THF and annealed; (**g**) G 12.8, S% 19.0, I% 79.0, cast from benzene. ε = per cent deformation of the specimen; σ = tensile stress.

Casting from THF seems to decrease dramatically the mechanical properties of copolymer **c**, as it appears from curve (**d**) in Figure 3. Annealing at 85°C under vacuum for 12 hours modifies substantially the mechanical properties of films cast from THF (Figure 3, curve **f**), improving the ultimate tensile stress from ca.30 MPa to ca.105 MPa, and the maximum strain from ca.50% to ca.200%. On the contrary, annealing of the same material cast from benzene (Figure 3, curve **e**) lowers its mechanical properties, reducing the ultimate tensile stress from ca.60 MPa to ca.45 MPa and the maximum strain from ca.350% to ca.150%.

These results, together with those of the DSC, suggest the possibility that the rigid polar EMA backbone and the rigid nonpolar polystyrene blocks can be dispersed, as distinct phases, within the rubbery polydiene. The modifications induced in the mechanical properties of the copolymer **c** by casting from solvents with different polarities and by annealing indicate that the distribution of such phases in the solid is very dependent on the formation conditions and on the thermal history of the specimens. Therefore, the complexity of such polyphasic materials makes very difficult to ascertain their actual microstructure by the analytical techniques used.

CONCLUSIONS

The experiments with model molecules, the IR spectra and the thermal analysis by DSC confirm that the coupling reaction between maleic anhydride copolymers and macrocarbanionic living ends occurs in the way previously postulated (4,5), i.e. quantitatively and without secondary reactions, and permits to obtain a great variety of materials only by varying the number and the composition of the reacting macrocarbanions. The most interesting graft copolymers appear to be those in which the grafts are diblock chains with an elastomeric block linked to the backbone and a rigid external one. In fact, the mechanical behaviour of the copolymers **c** and **g** suggests that, by varying the grafting degree and the relative lengths of the rigid and elastomeric blocks in the grafts, it can be possible to obtain materials with mechanical properties near to those given by thermoplastic elastomers. In addition, the materials synthesized by our method contain a great number of anhydridic or carboxylic groups, which can undergo further reactions leading to multifunctional copolymers, and/or be neutralized by bases to obtain materials with ionomeric properties.

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