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A. Bolognesi [a], M. Catellani [a] & S. Destri [a]
[a] ICM-C.N.R., Via Bassini 15/A, 20133, Milano, Italy
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SYNTHESES OF SOLUBLE GRAFT POLYACETYLENE COPOLYMERS°

A. BOLOGNESI,M. CATELLANI,S. DESTRI
ICM-C.N.R.,Via Bassini 15/A-20133 Milano-Italy

ABSTRACT Using two different synthetic routes,we have been able to obtain soluble forms of PA by grafting polyene chains onto a soluble polymeric matrix,namely polydiolefin.In order to get more information on the behaviour of the copolymer in solution,we have varied the following parameters:nature of the carrier,its molecular weight,PA content,temperature and solvent. We have obtained copolymer with PA content up to 50% in weight.

A new form of polyacetylene[1](PA) soluble in the usual organic solvents was obtained by grafting the polyenic chains onto a soluble polymeric matrix.This soluble PA may be interesting for further studies in the conducting polymer field and can give a more processable material.In fact after evaporation it's possible to get a film with an improoved air resistance and with a conductivity,upon doping,comparable to the insoluble PA.The copolymer solubility is probably due to a reduced interaction[2] among the polyenic chains and to the solvatation of the polydiolefin by the solvent.In this work we present two different synthetic routes to get soluble graft PA-polydiolefin copolymers.

Route A:The reaction between the catalytic system $Ti(OBu)_4/AlEt_3$ (1/4) and the vinyl side groups of the polymer carrier,leads to a titanium atom bonded to the matrix (step 1 Fig.1).A polyenic chain grows on this newly formed Ti-C bonds via successive insertions of acetylene (step 2 Fig.1). To prepare the supported catalyst

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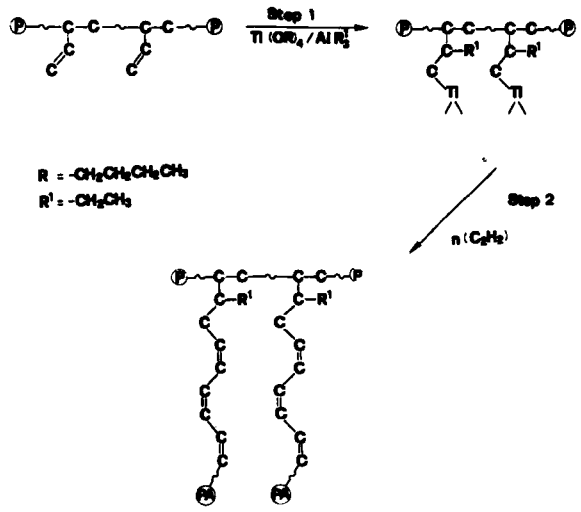

FIGURE 1 Scheme of route A

we have used the following polymers with side vinyl groups:polybutadiene (PB) 95% 1,4-cis,4% 1,2,1% 1,4-trans;polyisoprene (PI^+) 97.7% 1,4-cis,2,3% 3,4;polyisoprene (PI) 65.4% 1,4-cis,33,6% 3,4,1% 1,2. We have investigated the dependence of the solubility of graft copolymer PA-polydiolefin on the following parameters:type of carrier and its molecular weight,amount of catalyst,flow rate of acetylene.

TABLE I Solubility of the copolymers of different matrices.

Carrier	M_v	Physical state of the system
PB	112.000	Solution
PB	210.000	Solution
PI	700.000	Powder
PI^+	400.000	Gel
PI^+	900.000	Gel

Conditions of reaction:monomer flow rate:5 l/h;temp. 20°C; polymerization time 5 min;solvent toluene.

TABLE II % by weight of PA in the copolymer in dependence on the catalyst amount

Ti/1,2 units PB[a)]	0.06	0.1	0.2	0.3	0.43	0.84	1.0
PA %[b)]	12.6	19.8	23.4	26.2	37.9	51.0	precip.

a) Ratio between mmoles of Ti and mmoles of reactive 1,2 PB units

b) $\frac{\text{mg of PA}}{\text{mg of PA + mg of PB}}$ X 100 of soluble copolymer

An increase of the catalytic sites bonded to the carrier produces copolymer more rich in PA.When the (Ti/1,2 units)>.84,there are too many polyenic chains growing on the matrix so that the carrier loses its ability of carrying the graft PA in solution.Also the flow rate of acetylene affects the polymeric composition and therefore its solubility.This indicates that copolymer solubility depends on the number of growing polyenic chains and on their lengths.Preliminary data show that above 20°C on increasing the polymerization temperature the amount of the trans PA isomer increases.Soluble graft PA-PB copolymer can be obtained in aromatic and aliphatic hydrocarbons (toluene,benzene,heptane and cyclohexane).

Route B:We have formed carbanions on polydiolefinic matrix by means of Li-secBut in presence of tetramethylethylendiamine(Li/TMEDA=.9)[3]. These carbanions are capable of alkylating[4] $Ti(OBu)_4$ to give a Ti-C bond on which acetylene can insert to give the polyenic chain grafted on the carrier (Fig. 2).At low mmolesLi/mmoles diene units ratio (<.15) we observed the formation of carbanions,but not the subsequent transmetalation and the polymerization didn't take place. The best Li/Ti ratio in order to obtain a larger amount of grafted PA is 2/1 (see Table III).This finding together with the smaller percentage of unreacted free carrier can suggest that the number of grafting sites is increased with 2/1 ratio. These data are similar to those obtained by Fontanille[5] in the copolymerization of ethylene with polybutadienyllithium/$TiCl_4$ system.

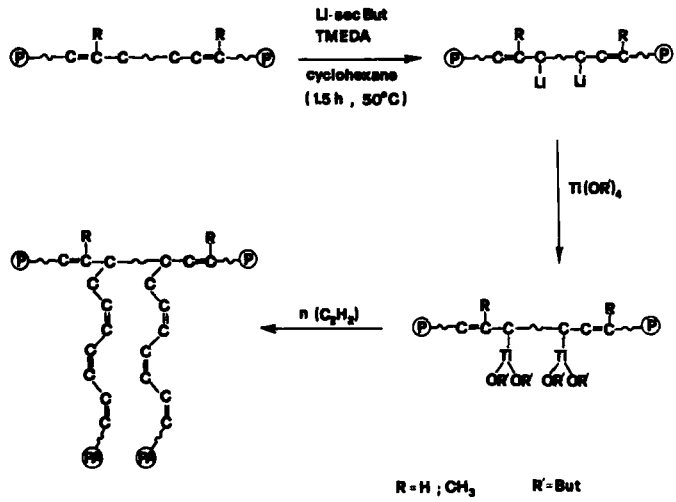

FIGURE 2 Scheme of route B

TABLE III PA percentage and ungrafted matrix[b] with different reaction conditions

Carrier	mmoles LisecBut / mmoles diene units	Li/Ti	%PA[a]	%ungrafted matrix[b]
PI	0.3	1	20	45
PI	0.3	2	25	40
PI	0.5	2	45	30

a) $\frac{\text{mg of PA}}{\text{mg of PA + mg of PI}} \times 100$

b) Recovered by extraction of the methanol copolymer precipitate with hot toluene.

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