Radical Reactivity of Olefin Copolymers with Vinyl Monomers*

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Investigations were made on the radical polymerization of styrene and of vinyl chloride in the presence of ethylene-propylene copolymers of n-heptane and of 3-methylhexane. The results obtained allowed us to calculate the transfer constants to the elastomer showing a good radical reactivity under the experimental conditions adopted.

As shown by recent works [1, 2] fragility of some resins, such as poly(vinyl chloride) or polystyrene, may be improved by using as reinforcing agents, graft copolymers of vinyl chloride and of styrene with olefin rubbers, *e.g.* saturated ethylene-propylene elastomers.

Graft copolymers of vinyl chloride and styrene with e.s.r. may be obtained by polymerizing the monomer in the presence of dissolved rubber when they are mutually soluble. A mixture forms consisting of a graft copolymer elastomer—vinyl polymer dispersed in the non grafted homopolymer matrix and of small amounts of non modified rubber.

Products of this type containing about 10% of total rubber are characterized by high values of impact strength, good processability properties, high resistance to ageing: they may be considered as products of industrial interest.

Most probably, in the case of saturated rubbers, the formation of graft copolymer in radical polymerizations, of elastomer—monomer initiator systems occurs through a chain transfer mechanism. The grafting active centres are originated by hydrogen atoms extraction from the elastomer chain by the action either of primary radicals from the initiator decomposition or of the macroradicals of the system derived from the monomer.

The aim of this work was the study of chain transfer reactions from reacting species to polyhydrocarbon for low values of the $\lceil s \rceil / \lceil M \rceil$ ratio.

We report the results obtained by studying the transfer reaction of styrene and of vinyl chloride concerning the ethylene-propylene copolymer and two low-molecular-weight hydrocarbons: *n*-hexane and 3-methylhexane, chosen as model substances of the units constituting polyhydrocarbon.

The systems studied must be considered initially homogeneous. In fact, at the molar ratios used, both copolymer and hydrocarbons are soluble in styrene and in vinyl chloride. In order to make negligible the formation of radical centres on the elastomer, caused

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by the initiator, we used as radical agent, AIBN, which, by thermal decomposition yields particularly stable radicals [3, 4] that cannot abstract hydrogen atoms from a olefin chain.

The values of the transfer constants of the vinyl monomer to the hydrocarbon compounds considered were calculated on the basis of *Mayo* equation [5]

$$rac{1}{ar{X}} = rac{1}{ar{X}_0} + C_{
m s} rac{[s]}{[M]},$$

where \overline{X} indicates the number average degree of polymerization obtained by viscosimetric measurements,

- [M] is the concentration in mole l^{-1} of monomer,
- [s] is the concentration in mole l^{-1} of the transfer agent,
- $C_{\rm s}$ indicates the constant of transfer.

Formula (1) does not consider the transfer to the initiator [6, 7] and to the homopolymet [8, 9] formed, being negligible, also because of the low concentration of the homopolymet under the polymerization conditions adopted by us.

To make comparable the results obtained in the presence of copolymer with those obtained in the presence of model hydrocarbons, the copolymer concentration was expressed by considering the six-atom groups contained in the polymer chain.

Experimental

Materials used

Copolymer C_2C_3 of Montecatini Edison purified by boiling acetone extraction for 172 hours with the following characteristics: Intrinsic viscosity determined in toluene at $30^{\circ}C = 1.43 \times 10^2$ cm³/g. Viscosimetric average molecular weight = $148 \times 10^{\circ}$ % w/w propylene (near i.r.) = 56.2° %. *n*-Hexane (Merck) — product fractionated on a distilling column. 3-Methylhexane (Fluka) — fractionated on a distilling column. Azobisisobutyronitrile (Fluka) — purum grade. Styrene (Montecatini Edison), stabilizerfree and distilled — purity 99.9%. Vinyl chloride (Montecatini Edison) — purity 99.9%

-All runs were carried out under nitrogen atmosphere at 65° C in the presence of AIBN (0.13%) calculated with respect to the monomer with conversions near 10%.

Polymerization of styrene was carried out in glass vials in a thermostatted bath equipped with a device for head-to-tail tumbling of the reaction mass.

Polymerization of vinyl chloride was carried out in a metal vial or in a stainless steel autoclave equipped with stirrer and jacket for circulation of the thermostatic liquid

Polymerization in the presence of C_2C_3 copolymer was preceded by polymer in monomer pre-dissolution.

Polystyrene and poly(vinyl chloride) prepared in the presence of *n*-hexane and of 3-methylhexane were separated from the reaction mixtures by pouring into an excess of methanol.

Separation of polystyrene and of poly(vinyl chloride) from the mixture obtained by polymerization of the monomers in the presence of C_2C_3 copolymer was carried out by extracting the reaction crude product with an excess of methyl ethyl ketone or dimethylformamide, that respectively dissolve polystyrene and poly(vinyl chloride).

Homopolymers were recovered from the diluted solution after concentration and precipitation in methanol.

Table 1

Transfer agent	Transfer agent [%]	Polymeri- zation [%]	[8] [M]	${\overline{M}}_{ m v}$	$rac{1}{ar{X}_{ extsf{v}}} imes 10^4$
n-hexane	0	8.80	0	136,300	7.6
	3.68	8.35	0.046	133,000	7.8
	7.48	7.80	0.095	131,300	7.9
	15.39	6.83	0.220	121,500	8.6
	42.11	3.97	0.880	90,640	11.5
	74.43	1.12	3.53	33,780	30.8
3-methylhexane	$3.83 \\ 7.76 \\ 15.92 \\ 33.55$	7.50 7.08 6.33 4.61	0.041 0.087 0.197 0.525	138,600 129,900 125,000 102,000	7.5 8.0 8.3 10.2
C ₂ C ₃ copolymer	2.00	8.00	0.025	134,800	7.7
	5.00	5.5	0.065	118,100	8.8
	10.00	3.6	0.138	111,800	9.4

Polymerization of styrene with various hydrocarbon transfer agents T 65°C; time of reaction 120 minutes; AIBN 0.13%

Table 2

Polymerization of vinyl chloride with various hydrocarbon transfer agents T 65°C; time of reaction 50 minutes; AIBN 0.13%

Transfer agent	Transfer agent [%]	Polymeri- zation [%]	[8] [M]	$\overline{M}_{ m v}$	$rac{1}{\overline{X_{ m v}}} imes 10^3$
n-hexane	0 5.00 9.10 20.00 50.00	13.0 12.1 11.9 9.9 5.0	0 0.038 0.072 0.180 0.726	56,300 50,580 45,620 40,290 19,240	$1.1 \\ 1.2 \\ 1.4 \\ 1.6 \\ 3.2$
3-methylhexane	8.85 12.15 33.0	11.0 9.6 14.0	$0.061 \\ 0.086 \\ 0.307$	39,870 39,750 40,290	$1.6 \\ 1.6 \\ 1.6$
C ₂ C ₂ copolymer	$2.00 \\ 5.00 \\ 10.00 \\ 15.4$	10.3 8.1 6.9 20	0.015 0.039 0.082 0.134	59,830 59,340 56,300 49,000	1.0 1.1 1.1 1.3*

^{*}Reaction time 105 minutes. Polymerization carried out in the presence of a lowmolecular-weight C₂C₃ copolymer having: 56% C₃ and intrinsic viscosity determined in toluene at 30°C 0.46 \times 10² cm³/g. Viscosimetric average molecular weight 27 \times 10³. Intrinsic viscosities were measured at 30°C using toluene as solvent for polystyres, and cyclohexanone for poly(vinyl chloride). The average molecular weight was calculated by formula $[\eta] = K M^a$ using the following constants

polystyrene	$K=1.1 imes10^{-4}$	a = 0.725 ,	[10]
poly(vinyl chloride)	$K=1.63 imes10^{-4}$	a = 0.770.	fır

Results

Table 1 summarizes the results of measurements carried out in order to calculate the values of the transfer constants reported in the first column of Table 3 for the styremetransfer agent.

The results obtained show that the copolymer is a more effective transfer agent th_{RB} *n*-hexane and 3-methylhexane.

Table 2 shows the results obtained by studying the polymerization of vinyl chloride in the presence of the same chain transfer agents. When using 3-methylhexane (see also Table 2), regular variations of the viscosimetric average molecular weight have not been detected on varying the concentration of the transfer agent.

Table 3

Transfer constants for various hydrocarbons with styrene and vinyl chloride at 650

Transfer agent	Monomer		
Transier agent	styrene	vinyl chloride	
n-hexane	$0.4 imes10^{-3}$	$2.9 imes10^{-3}$	
3-methylhexane	$0.6 imes 10^{-3}$	_	
C_2C_3 copolymer	$1.5 imes 10^{-3}$	$2~ imes~10^{-3}$	

From the results obtained in the presence of *n*-hexane or of C_2C_3 copolymer, we could calculate the relating transfer constants reported in the 2nd column of Table 3.

The values of the transfer constants that may be calculated in the previous cases here just an apparent meaning in that the polymerization proceeds with precipitation of poly (vinyl chloride) and a simple interpretation of transfer phenomena in a heterogeneous system is rather difficult.

In any case, the experimental points collected in Tables 1 and 2, if plotted in a l/X_1 graph vs. [s]/[M] are well lined up according to straight lines, the slope of which allows the calculation of the value of C_5 .

The order of magnitude of the transfer constants is the same when the agent is the C_2C_3 copolymer or *n*-hexane: its value is not high and this explains the relatively low grafting yield, by operating with monomer excess.

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