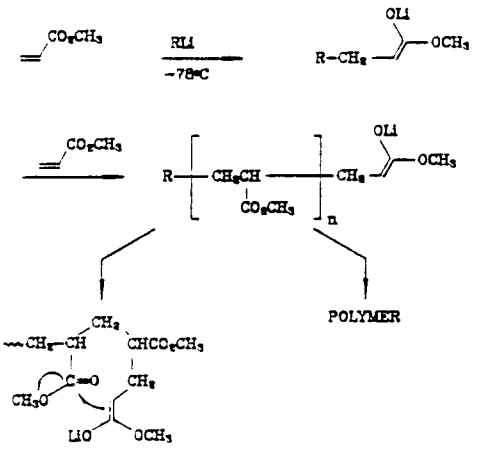
ANIONIC POLYMERIZATION



THE IDEAL POLYMERIZATION

1) Quantitative yield

2) Readily accessible initiator

3) Control of MW

4) Narrow molecular weight distribution
   $D = M_W/M_N < 1.2$
   M_W = weight average molecular weight
   M_N = number average molecular weight

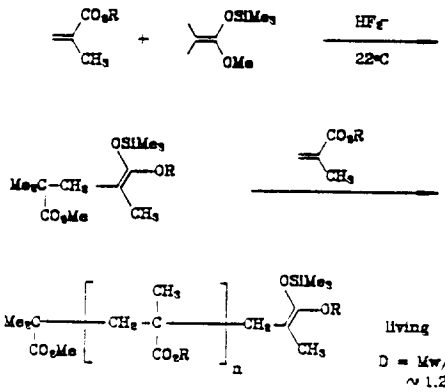
5) Living polymer

6) Room temperature

7) Stereoselective (tacticity)

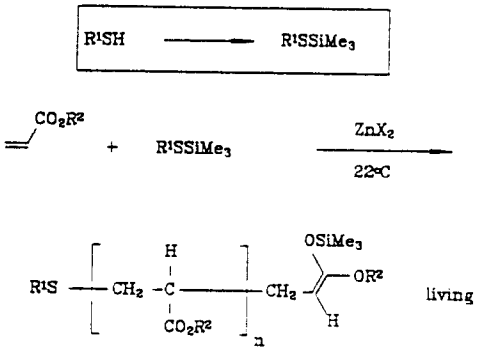
8) Functionalized ends

GROUP-TRANSFER-POLYMERIZATION
(DUPONT)

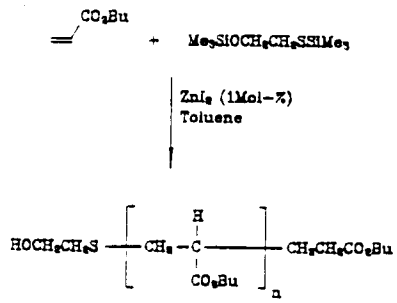


O.W. Webster.etal.J.Am.Chem.Soc.
105,5706(1983)

ALKYLTHIOSILANES AS INITIATORS

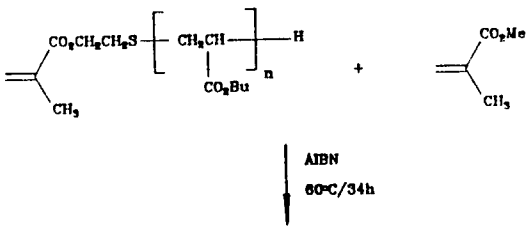


FUNCTIONALIZED INITIATORS

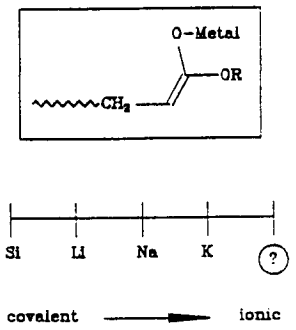


M_n(exp.) = 14.2Kg/mol
M_w = 15.3kg/mol
D = 1.08

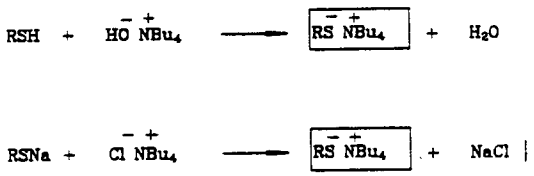
RADICAL COPOLYMERIZATION



DEGREE OF COVALENCY

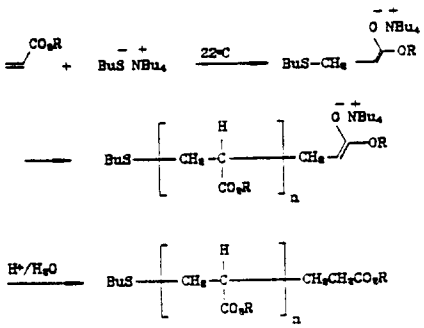


AMMONIUM-THIOLATES



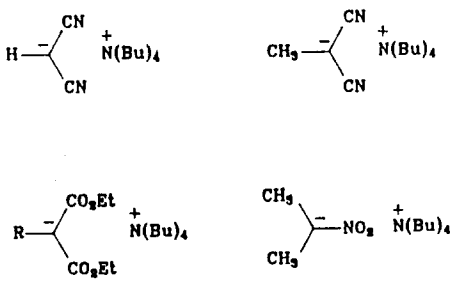
R = n-Alkyl,Aryl

METAL-FREE ANIONIC POLYMERIZATION



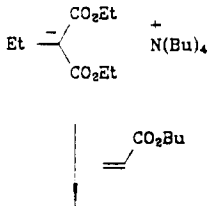
- quantitative conversion !

INITIATORS



R = CH_3, C_6H_5

EXAMPLE

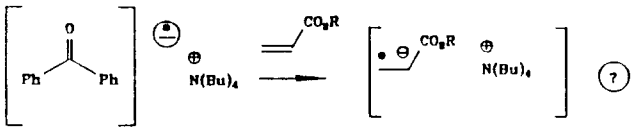


Polybutylacrylate (100%)

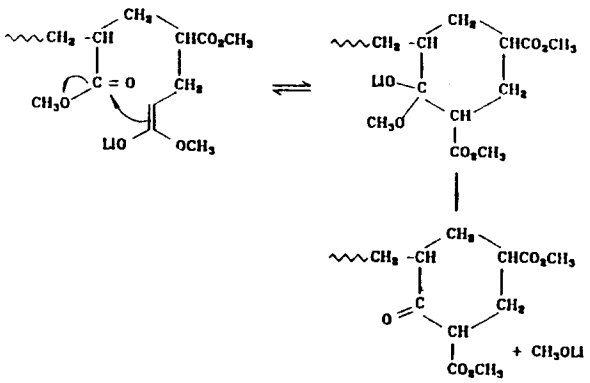
M_n(exp.) = 1.79kg/mol [M_n(calc.) = 1.47]
M_w = 2.03kg/mol
D = 1.18

M_n(exp.) = 11.08 [M_n(calc.) = 10.4]
M_w = 13.19
D = 1.19

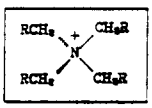
AMMONIUM RADICAL–ANIONS AS INITIATORS



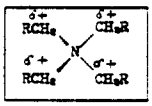
CLAISEN–CONDENSATION AS CHAIN TERMINATION



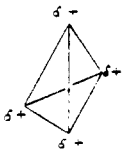
MO–CALCULATIONS



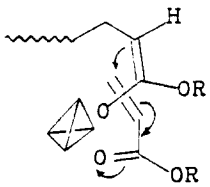
formal



correct

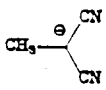
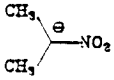


TRANSITION STATE



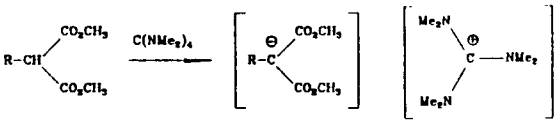
ACRYLONITRILE

3 mmol initiator in 20 ml THF
monomer dissolved in 20 ml THF

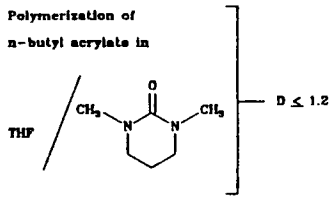
initiator	mmol AN	M_n(calc)	solution
	30	0.61	homogeneous
	60	1.14	homogeneous
	120	2.20	heterogeneous
	similar as above		

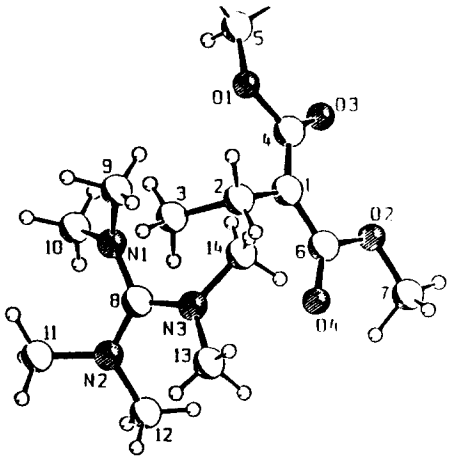
CARBOCATIONS AS COUNTERIONS

EXAMPLE

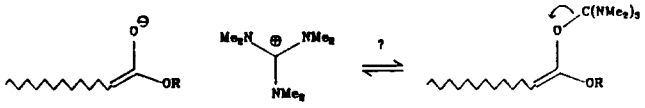


Polymerization of n-butyl acrylate in THF

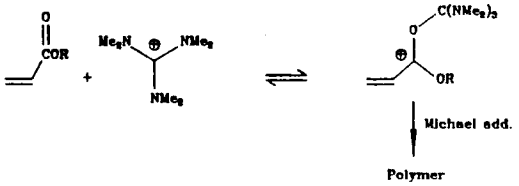




NATURE OF CHAIN END



AUTOCATALYSIS ?



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