affecting the maximum yield. This is apparently the result of obtaining a maximum ratio of the rate of chain propagation to that of total reaction rate under optimum conditions.

CONCLUSIONS

The production of a polycarbonate from di-(4-hydroxyphenyl)-phenylmethane and phosgene was studied. The optimum synthesis conditions and the influence of some of the factors on yield and specific viscosity were determined.

Translated by K. A. ALLEN

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RELATIVE REACTIVITIES OF 2-CHLORO- AND 2,3-DICHLORO-1,3-BUTADIENES, AND SOME OF THE PROPERTIES OF THEIR COPOLYMERS*

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THE monomer 2,3-dichloro-1,3-butadiene has recently been the centre of much attention because of the valuable properties of its copolymers with 2-chloro-1,3-butadiene (chloroprene).

It appears that some of these copolymers will soon be produced on an industrial scale. A comparative study of the reactivities of these two monomers during copolymerization was therefore of interest.

We have not been able to find any reference in the literature to the relative reactivities of chloroprene (CP) and 2,3-dichloro-1,3-butadiene (DCB).

EXPERIMENTAL

CP and DCB were copolymerized in an aqueous emulsion using a resinate/sodium dodecyl sulphate mixture as the emulsifier. The polymerization initiator was potassium persulphate. All operations were carried out in an argon atmosphere. The conversion of the monomers was determined from the specific weight of the latex using a measuring arheometer with a 0·001 g/cc scale of division. The monomers were vacuum-distilled before polymerization; their properties were as follows: $CP = d_4^{20}$ 0·9570; n_D^{20} 1·4586; $DCB - d_4^{20}$ 1·1810; n_D^{20} 1·4881.

The polymerizations were carried out at $40\pm1°C$; the ratio of monomers was varied from $1:0$ to $0:1$.

To calculate the relative reactivities of the monomers, the copolymer composition was determined at different degrees of conversion and at different monomer ratios in the starting emulsion. The copolymer composition was assessed on the basis of its chlorine content determined by the Karius method.

The relative reactivities (copolymerization constants) were calculated by using the integrated equation of Mayo and Lewis [1]; the results are given in Table 1.

The average r_1 and r_2 values were found by graphic methods and they were: $r_1=0·335 \pm0·055$ (CP); $r_2=2·15\pm0·25$ (DCB).

TABLE 1. RELATIVE REACTIVITIES OF CP (M_1) AND DCB (M_2)

| Molar content of monomers in start emulsion		% polymerization	Molar content of unreacted monomers		P	Relative reactivities of monomers (as coordinates of curve)	
$M_1°$	$M_2°$		M_1	M_2		r_1	r_2
0·8	0·2	25	0·645	0·105	−2	0·294	2·414
					−4	0·372	3·51
					−5	0·398	4·01
0·5	0·5	50	0·317	0·183	−1	0·216	1·784
					−2	0·42	2·16
					−3	0·572	2·28
0·75	0·25	55	0·409	0·041	−1	0·257	1·743
					−2	0·301	2·398
					−3	0·347	2·966
0·677	0·333	30	0·52	0·180	−1	0·282	1·718
					−2	0·375	2·25
					−3	0·446	2·63
0·25	0·75	50	0·174	0·326	−2	0·335	2·33
					−3	0·505	2·475
					−4	0·605	2·58

It follows from these values that DCB is much more reactive than CP considering both types of polymer radicals; the DCB radical reacted 2·15 times more readily with its own monomer than with CP. As to the CP radical, its reactivity with its own monomer was only one-third compared with that involving DCB. The copolymer will therefore become enriched with DCB in the initial stage of copolymerization compared with the content of monomers in the starting mixture.

As a result of the lower reactivity of CP, DCB will be utilized much faster than CP, which makes DCB stand out amongst monomers such as styrene or acrylonitrile, these remaining in the free state (about 70%) on completion of their copolymerization with CP.

The probability of the formation of macromolecular M_1—M_1, M_1—M_2 and M_2—M_2 bonds due to the specificity of the respective elementary reactions in the total rate of the process of macromolecular growth was calculated on the basis of the obtained copolymerization constants [2].

The probability was calculated by using the approximation given by Abkin and Medvedev [3, 4] for systems with different monomer ratios in the starting emulsion and for a 50% conversion of CP to the polymer.

The results of these calculations are given in graph form above; one can see that an initially small DCB content will give DCB chains mainly consisting of a single monomer unit in the macromolecule, while the CP chains will consist of several monomer units. An increase of the amount of DCB present will greatly increase the number of DCB units in the chain.
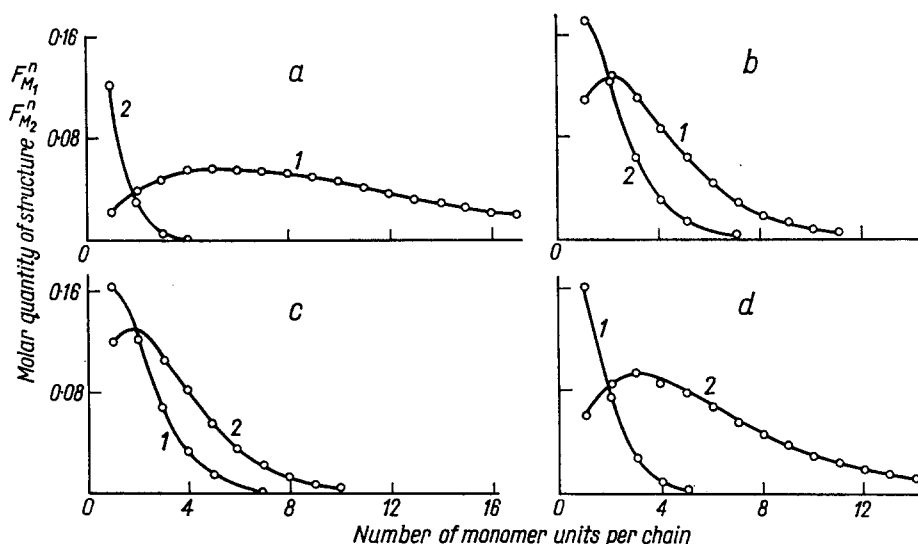
Chain distribution in the copolymer macromolecule at CP : DCB molar ratios of, $a - 92 \cdot 5 : 7 \cdot 5$; $b - 76 \cdot 5 : 23 \cdot 5$; $c - 58 \cdot 2 : 41 \cdot 8$; $d - 41 \cdot 6 : 58 \cdot 4$. $1 - $CP (M_1); $2 - $DCB (M_2).

SOME OF THE PROPERTIES OF THE CP–DCB COPOLYMER

Depending on the ratio of monomers in the starting mixture, the copolymers can either be elastomers or plastics.

The Table 2 shows that a larger content of DCB chains in the copolymer reduced the frost-resistance and physico-mechanical properties, but improved its flame- and benzene-fat-resistance. The improved flame-resistance was in this case due to the larger chlorine content of the copolymer.

A very interesting property of the CP–DCB copolymers was their improved dielectric constants when compared with CP, i.e. specific electrical resistance (ρ_v) and tangent angle of dielectrical loss (tan δ).

As a result of these findings, CP–DCP copolymers promise well as materials for cable production by combining insulating and protective properties.

CONCLUSIONS

(1) The copolymerization constats for the monomer pair 2-chloro- and 2,3-di-chloro-1,3-butadiene were calculated.

(2) The properties of the copolymers are described.

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TABLE 2. PROPERTIES OF CP–DCB COPOLYMERS PRODUCED AT DIFFERENT MONOMER RATIOS IN THE STARTING EMULSION

DCB content, % w/w	Karrer plasticity	Physico-mechan. properties of vulcanizates not filled			swelling capacity in a petrol–benzene mixture (3 : 1) % w/w	Flame resistance, sec	Brittleness temp., °C	Dielectr. const.		Remarks
		fracture stress, kg/cm²	rel extension, %	% resid. extension				ρ ohm×cm	tan δ	
0	0·67	200	900	16	75	burns completely	−38	7×10^{11}	0·032	Almost 100% conversion of monomers to polymer
5	0·68	210	890	16	72	ditto	−36	4×10^{12}	0·011	
10	0·67	200	880	15	70	30	−36	4×10^{12}	0·012	
20	0·69	195	850	13	68	10	−31	5×10^{12}	0·013	
30	0·67	170	840	12	68	3	−27	2×10^{13}	0·013	
40	0·66	163	840	12	67	3	−23	3×10^{13}	0·014	The ratio of monomer chains present in the polymer is proportionate to their ratio in the mixture at the start
50	0·67	152	820	12	66	1	−20	$5·9 \times 10^{13}$	0·027	
60	Could not be determined				66	1	−14	$6·2 \times 10^{13}$	0·030	
70	Ditto				57	0	− 5	$8·3 \times 10^{13}$	0·033	
80					26	0	+ 5	$5·3 \times 10^{14}$	0·033	

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CONNECTION BETWEEN THE HETEROPHASE COPOLYCONDENSATION CONSTANTS AND THE ADSORPTION CHARACTERISTICS OF MONOMERS*

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THE copolymerization method widely used in the chemistry of high polymers can give important information about the mechanism of the reaction components by analysis of the copolymerization constants.

The quantitative aspects of the copolycondensation method are not fully developed at present. Although a start was made [1] by publishing information on the calculation of the copolymerization constants for different variants of heterophase copolycondensations [2–4], the values obtained were only used to draw qualitative conclusions regarding the characteristics of the mechanisms of the respective processes.

By using very general theories about the mechanism of the processes occurring at the boundary surface, one can quantitatively assess the physical meaning of the copolycondensation constants of the heterophase variants of the processes (interfacial and gas-phase polycondensation).

Where the reaction takes place only at the interface and is not complicated by reactions in space (of the phases), the composition of the copolymer will be determined by the concentrations of reagents A and B present in the reaction zone, i.e. at the interface. When surface-active monomers are used, the concentrations of A and B in the boundary layer will differ from those present in the solution and can be represented by the Boltzman equations [5]:

$$[A]' = [A] \times e^{-E_A/RT} \tag{1}$$

$$[B]' = [B] \times e^{-E_B/RT} \tag{2}$$