Effect of light and solvent polarity on the preparation of polyisobutylene and of the copolymer of isobutylene with isoprene in the presence of VCl_4

L. Toman and M. Marek
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 00 *Prague* 6, *Czechoslovakia*
(*Received* 27 *February* 1981)

The polymerization of isobutylene and the copolymerization of isobutylene with isoprene, in the presence of VCl_4 in heptane and methyl chloride, were investigated in the temperature range from 253–195K in the dark and with the effect of visible light. It was found that, in the polymerization of isobutylene, the molecular mass increased linearly with decreasing temperature (log $\bar{M}\eta$ vs. $1/T$). In the copolymerization of isobutylene with isoprene, it was found that the molecular mass of the copolymer increased linearly with decreasing temperature (log $\bar{M}\eta$ vs. $1/T$) in methyl chloride, while in heptane there was a break in continuity near 238–233K. In the copolymerization in methyl chloride, isoprene reduced the molecular mass of the copolymer compared with that of polyisobutylene alone but, in heptane with the effect of light, isoprene increased the molecular mass of the copolymer up to twice that of polyisobutylene prepared under the same experimental conditions. If the copolymerization took place in methyl chloride, the unsaturation in mol% was equal to half the mol% content of isoprene in the initial monomeric mixture, while unsaturation of the copolymers formed in heptane solution was somewhat higher than the mol% content of isoprene in the mixture of monomers. Light had no effect on the molecular mass of polyisobutylenes and unsaturation of copolymers. VCl_4 appeared to be a highly effective initiator of the polymerization of isobutylene and of the copolymerization of isobutylene with isoprene.

INTRODUCTION

One component of the coordination catalyst in the synthesis of polyolefins is frequently $TiCl_4$ or VCl_4. Only $TiCl_4$ has so far been used in the cationic polymerization, while VCl_4 has failed to attract any major attention. Literature[1–3] suggests that VCl_4 ranks among the so-called 'inactive' Lewis acids, along with $TiCl_4$, $SnCl_4$, which do not initiate the polymerization of isobutylene in the absence of coinitiators. With respect to the molecular masses of polyisobutylenes prepared by using various Lewis acids, VCl_4 was regarded[4] as a weak initiator, together with $SnCl_4$ and $FeCl_3$.

At the beginning of the seventies we detected the effect of light on the polymerization of isobutylene in the presence of VCl_4 alone[5]; we found that isobutylene formed charge-transfer complexes with VCl_4 in the reaction system[6], which, after excitation with light, were able to initiate the polymerization of isobutylene. The initiation step proceeds via radical cations of the monomer[7].

We have demonstrated[8] that the polymerization of isobutylene carried out in a nonpolar medium can also be initiated in the dark by adding 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, styrene, alpha-methylstyrene or *p*-divinylbenzene. We have also found[8] that in the copolymerization of isobutylene with butadiene or isoprene in the presence of VCl_4 light, the polarity of the solution affects the properties of the copolymer formed. In copolymerizations in heptane with the effect of light, the copolymers formed are soluble in CCl_4, benzene, heptane, while copolymers arising in the dark are insoluble. In methyl chloride, soluble copolymers are formed independently of the procedure used for the copolymerization (in the dark or with light). The isoprene[9] and butadiene[10] units are incorporated into the polymer chain of soluble copolymers by 1,4-addition. This paper reports further results obtained in the investigation of the polymerization of isobutylene and copolymerization of isobutylene with isoprene in the presence of VCl_4.

EXPERIMENTAL

Materials and their purification

Isoprene produced by the Koch-Light Laboratories Ltd. was rectified under argon on a column containing 30 TP and dried on molecular sieves (Potasit 3, Czechoslavak origin). Before use, isoprene was redistilled from sodium in a stream of argon. Isobutylene, purity 99.8%, manufactured by Hüls, was dried by standing with sodium wire in a glass pressure ampoule. Heptane was purified by shaking with a mixture of sulphuric acid and phosphorus pentoxide[11], rectified in a stream of argon and dried by standing over sodium wire. Methyl chloride was purified by passing through a column containing concentrated sulphuric acid and predried on a column with $CaCl_2$. After that it was dried by standing over molecular sieves in a pressure glass ampoule. Argon, freed from oxygen, was dried with molecular sieves and sodium hydride. The moisture content of isobutylene, isoprene, heptane, methyl chloride and argon measured with a

0032-3861/81/091243-07$02.00

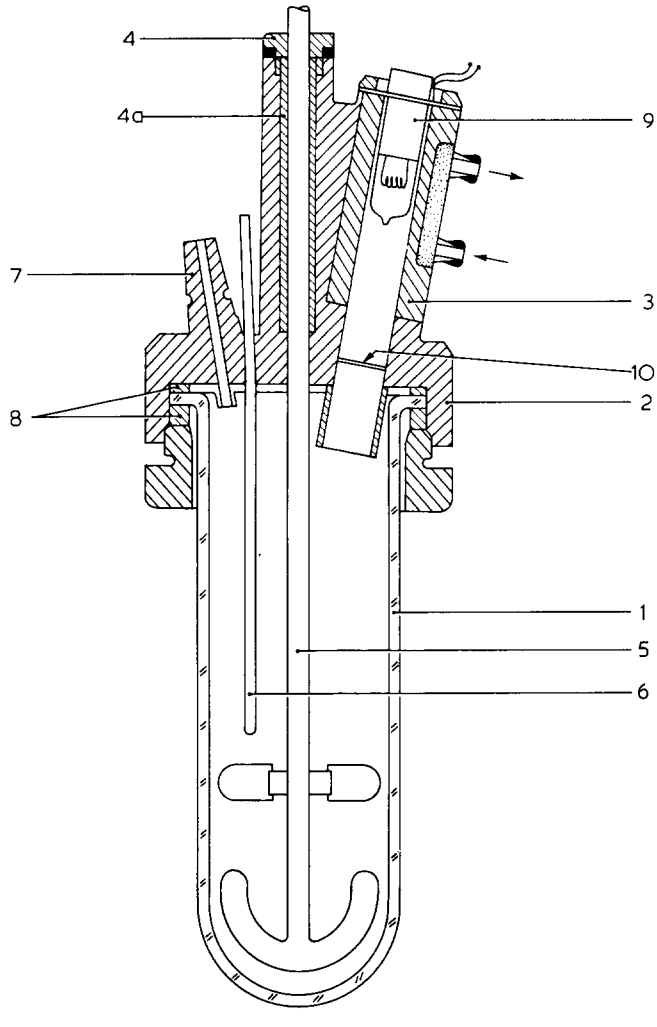


Figure 1 Photopolymerization reactor

Shaw hydrometer did not exceed 3 ppm H_2O. VCl_4 (Kodak, London) used was commercially pure. Solutions of VCl_4 in heptane were kept in glass ampoules with a three-way cock under argon in the dark at 255K.

Polymerization and photopolymerization reactor

The polymerizations and copolymerizations were performed in a reactor[12] shown in *Figure 1*. The reactor consists of a glass vessel (1) and a metal head (2), with the liquid-cooled lighting equipment (3) which contains also the bearing (4) of a stirrer (5) with a specially adjusted packing (4a), a thermocell jacket (6) and a tube adjusted to the three-way cock for the inlet of reaction components in a stream of argon (7). The head is tightly connected with the glass reactor vessel by packing (8). In such a reactor the reactions could be carried out under strictly dry conditions in an argon atmosphere. The tube of the lighting equipment contained a commercial car-type halogen bulb H3 (Czechoslovak origin), 12V, 55W (9), separated from the reaction space with packed quartz glass (10). The reactions were carried out in the reactor in the dark and with the effect of visible light. When the reaction occurred in the dark, the reactor was covered with a black case before the addition of the initiator to the reaction mixture. In the polymerization with the effect of light, the reaction mixture was irradiated in the reactor after the initiator had been added, but only during the induction period; after that, the light was switched off, the reactor was covered and the polymerization proceeded in the dark. If the irradiation continued after the induction period, the light did not affect the properties of the eventual polymer or copolymer ($\bar{M}\eta$, unsaturation); it only increased the rate of the reaction. For this reason, in all experiments involving photochemical polymerization or copolymerization, the irradiation took place only during the induction period.

The concentration of the initiator VCl_4 was 3.6×10^{-4} mol l^{-1} for reactions in methyl chloride and 1.1×10^{-3} mol l^{-1} for those in heptane. The homopolymerizations of isobutylene proceeded in methyl chloride or heptane, the monomer concentration was 7.0 or 4.94 mol l^{-1}.

The copolymerizations of isobutylene with isoprene were performed in methyl chloride with the total concentration of monomers ranging from 5.45 to 9.1 mol l^{-1}, and from 2.5 to 10.6 mol l^{-1} for reactions in heptane. The isoprene content in the monomeric mixture isobutylene–isoprene varied in the range from 0.15 to 4.1 mol l^{-1} for reactions in methyl chloride and from 0.2 to 3.3 mol l^{-1} for reactions in heptane.

In heptane all polymerizations of isobutylene or copolymerizations of isobutylene with isoprene were carried out with the effect of visible light; in methyl chloride, they were carried out both in the dark and with the effect of light. The polymerization and copolymerizations were terminated by adding ethanol (1 ml); polymer samples were obtained after the removal of volatile fractions at reduced pressure (0.5 Pa at 313K).

Determination of the molecular weight and unsaturation of copolymers

The molecular masses of polymeric products obtained were determined viscometrically in heptane at 293K[13]. The unsaturation of the copolymers was determined ozonometrically.

RESULTS

Course of the polymerization reaction

The polymerization of isobutylene and copolymerization of isobutylene in the presence of VCl_4 proceeded with an induction period. In the investigated temperature range from 195 to 253K, at the same concentration of initiator the induction period depends on the concentration of the monomer, polarity of the medium and route of the reaction (in the dark or with the effect of light). In methyl chloride, the polymerization and copolymerization proceeded in the dark spontaneously, and the induction period became longer with increasing concentration of the monomer. Thus, at the monomer concentration 5.45 mol l^{-1}, the period was ~0.15 min and at 9.1 mol l^{-1} it was ~1 min. With irradiation the reactions proceeded shortly after the mixture had been irradiated. The induction period lay in the range 3–5 s. In heptane solution the polymerization and copolymerization with the effect of light also proceeded with an induction period, but the period became longer with decreasing concentration of the monomers. At the monomer concentration 10.6 mol l^{-1} the induction period was ~10 min, at 2.5 mol l^{-1} it was ~15 min.

Polymerization of isobutylene

The effect of temperature on the molecular mass of polyisobutylene was investigated in the temperature

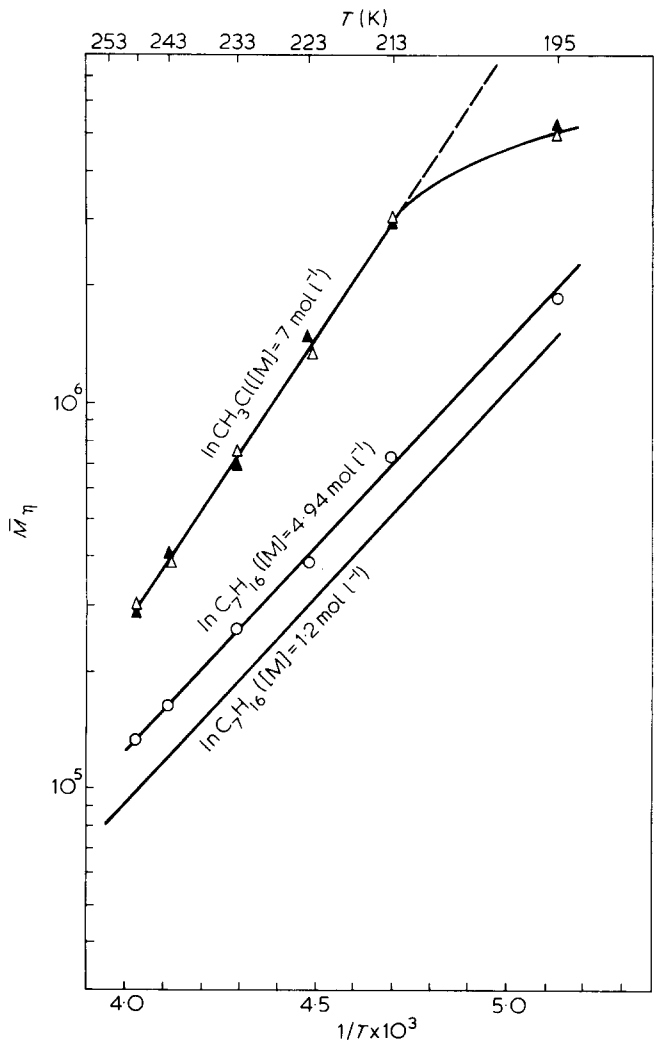


Figure 2 Polymerization of isobutylene in heptane and methyl chloride: log $\bar{M}\eta$ vs. $1/T$ dependence. In methyl chloride ([VCl_4] = 3.6×10^{-4} mol l^{-1}) the polymerizations were carried out in the dark (▲) and with irradiation (△) and conducted up to 20–25% conversion; in heptane ([VCl_4] = 1.1×10^{-3} mol l^{-1}) the polymerizations were carried out with irradiation and conducted up to 15–20% conversion (○)

range from 353 to 195K. The results are presented in *Figure 2*. A linear log $\bar{M}\eta$ *versus* $1/T$ dependence was obtained in the heptane solution within the whole temperature range; it was shifted in parallel towards higher molecular masses compared with the dependence described earlier[13] for heptane solutions with a lower monomer content and a higher concentration of the initiator ([M] = 1.2 mol l^{-1}; [VCl_4] = 8×10^{-3} mol l^{-1}. In methyl chloride, the linear log $\bar{M}\eta$ *versus* $1/T$ dependence was the same both in the dark and with the effect of light in the temperature range 253–213K. At 195K, the molecular masses of polyisobutylenes were somewhat lower than would correspond to the linear dependence of log $\bar{M}\eta$ on $1/T$. The approximate overall activation energies of the degree of polymerization (E_{DP}) for polymerizations in heptane and methyl chloride were determined from the Arrhenius diagram log $\overline{DP}$ vs. $1/T$.

The E_{DP} value for polymerizations in methyl chloride was somewhat higher ($\sim E_{DP} = -28.7$ kJ mol^{-1}) than for polymerizations in heptane solutions ($\sim E_{DP} = -20.2$ kJ mol^{-1}). For the sake of comparison, we give here the value of E_{DP} determined by Kennedy and Squires[14] ($\sim E_{DP} = -23.4$ kJ mol^{-1}) for the polymerization of isobutylene in methyl chloride with BF_3, $AlCl_3$ and $EtAlCl_2$ as initiators.

Copolymerization of isobutylene with isoprene

Effect of temperature: As in the polymerization of isobutylene alone, the molecular masses of copolymers obtained in the copolymerization of isobutylene with isoprene increase with decreasing temperature within the whole temperature range under investigation (*Figure 3*). In methyl chloride, a linear log $\bar{M}\eta$ *versus* $1/T$ dependence was obtained in the temperature range from 253 to 213K, and was found to be the same for copolymerizations both in the dark and with the effect of light. The calculated value of the approximate overall activation energy E_{DP} is ~ -28.0 kJ mol^{-1}. The unsaturation of the copolymer was ~ 1.5 mol % within the whole investigated temperature range and was independent of the effect of light.

The log $\bar{M}\eta$ *versus* $1/T$ dependence obtained in heptane solution within the temperature range 253–195K had a break in the range from 238 to 233K. One can see that this

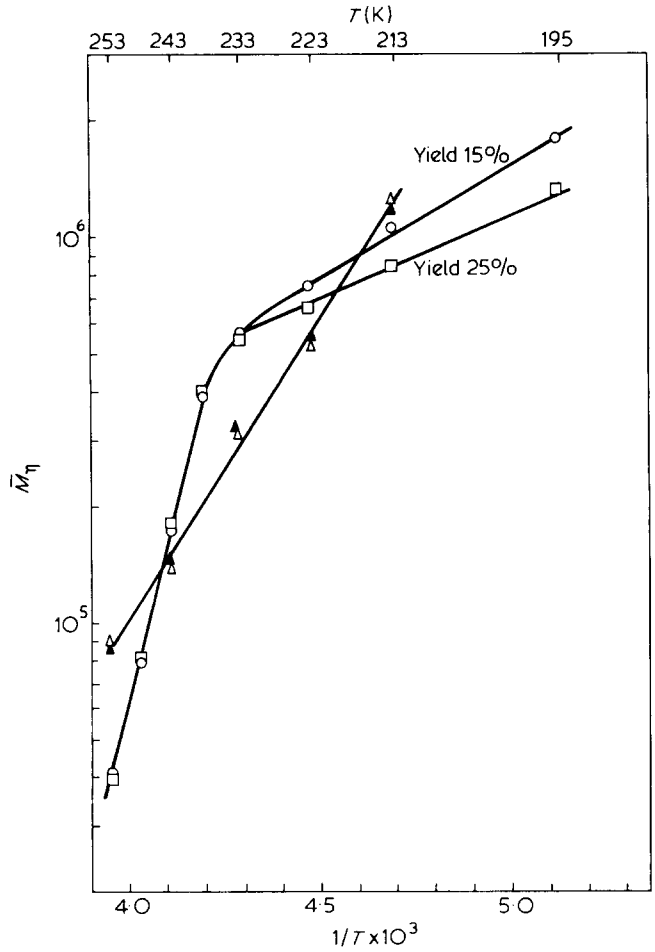


Figure 3 Copolymerization of isobutylene with isoprene in heptane and methyl chloride; log $\bar{M}\eta$ vs. $1/T$ dependence. In methyl chloride ([VCl_4] = 3.6×10^{-4} mol l^{-1}, [isobutylene] = 7.0 mol l^{-1}, [isoprene] = 0.216 mol l^{-1}) the copolymerizations were carried out in the dark (▲) and with the effect of light (△) and conducted up to 20–25% conversion, the unsaturation of the copolymer was ~1.5 mol%. In heptane ([VCl_4] = 1.1×10^{-3} mol l^{-1}, [isobutylene] = 4.940 mol out with the effect of light copolymerizations were carried out with out with the effect of light and conducted to 15% (○) and 25% (□) conversion, the unsaturation of the copolymer was ~2 mol%

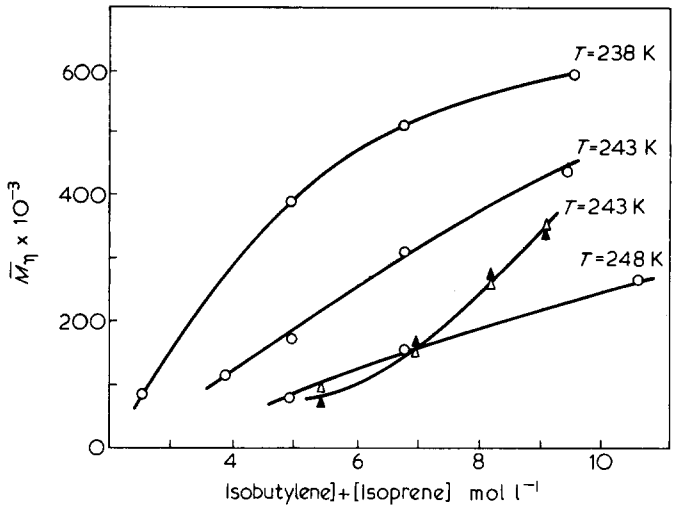


Figure 4 Copolymerization of isobutylene with isoprene in heptane and methyl chloride. The effect of the total concentration of monomers on the molecular mass of the copolymer at a constant mol% isoprene content in the mixture of monomers: [isoprene]/([isobutylene] + [isoprene]) = const. = 1.65 mol% for heptane and 3.0 mol% for methyl chloride. In heptane, the copolymerizations were carried out with irradiation (○) at 238, 243 and 248 K, conversion from 15–20%; in methyl chloride, they proceeded in the dark (▲) and with irradiation (△) at 243 K, conversion from 20 to 25%. The unsaturation of the copolymers prepared in heptane was ~2 mol% and in methyl chloride was ~1.5 mol%. The concentrations of the initiator were the same as in *Figure 3*

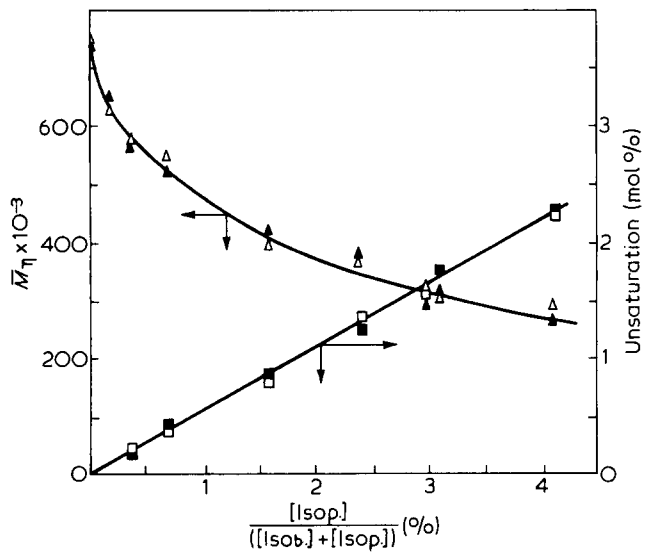


Figure 5 Copolymerization of isobutylene with isoprene in methyl chloride at 233 K. The effect of isoprene on the molecular mass and unsaturation of the copolymer at a constant total concentration of monomers: [isobutylene] + [isoprene] = const. = 7.0 mol l^{-1}. The copolymerizations were conducted from 20 to 25% conversion, concentration of the initiator was the same as in *Figure 3*; molecular masses (▲) and unsaturation (■) of copolymers prepared in the dark, (△) and with irradiation, (□)

dependence is linear at higher temperatures in the range from 253 to 238K. For this temperature range E_{DP} is ~ -57.4 kJ mol^{-1}. At lower temperatures, i.e. in the range from 233 to 195K, E_{DP} calculated from this linear dependence is ~ -11.3 kJ mol^{-1} (for copolymerizations conducted to 15% conversion). To find out to what extent the molecular mass of the copolymer varies depending on temperature, we determined molecular masses reached at 15 and 25% conversion. These have been plotted as a function of $1/T$ (*Figure 3*). The dependence shows that the molecular masses of copolymers reached at two different conversions are the same for the given temperature of polymerization (temperature 233K and above). The differences in molecular masses can be observed only at 223K and below.

Effect of the total concentration of monomers: The effect of the total concentration of monomers on the molecular mass of the copolymer in heptane solution was investigated at 248, 243 and 238K and in methyl chloride at 243K. The isoprene content in the injected mixture of monomers was kept constant [isoprene]/([isobutylene] + [isoprene]) and was 1.65 mol % for heptane solutions and 3 mol % for copolymerizations in methyl chloride. The dependences are given in *Figure 4*. At all the temperatures used the molecular mass of the copolymer depended directly on the concentration of monomers. In methyl chloride the molecular mass of the copolymer was independent of light.

Effect of isoprene concentration: The effect of isoprene concentration on the molecular mass and unsaturation of the copolymer was investigated in heptane solution at 238K, and in methyl chloride at 233K. The results are summarized in *Figures 5* and *6*.

Since the molecular mass of the copolymer depends on the concentration of the monomer, the total concentration of monomers in the injected solution was kept constant; Σ[isobutylene] + [isoprene] = 4.94 mol l^{-1} for heptane solutions and 7.0 mol l^{-1} for copolymerizations in methyl chloride. In methyl chloride (*Figure 5*), the molecular mass of the copolymer formed decreases with increasing concentration of isoprene in the injected solution. The unsaturation increases linearly, being approximately equal to half the content (mol %) of isoprene in the injected solution of monomers. Different techniques

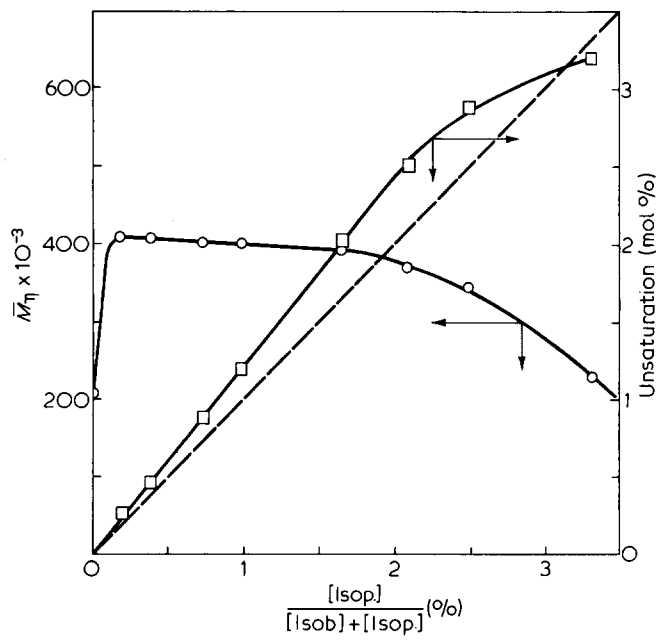


Figure 6 Copolymerization of isobutylene with isoprene in heptane at 238 K. The effect of isoprene on the molecular mass (○) and unsaturation (□) of the copolymer at a constant total concentration of monomers: [isobutylene] + [isoprene] = const. = 4.94 mol l^{-1}. The copolymerizations were carried out with irradiation and conducted up to 15–20% conversion. The concentration of the initiator was the same as in *Figure 3*

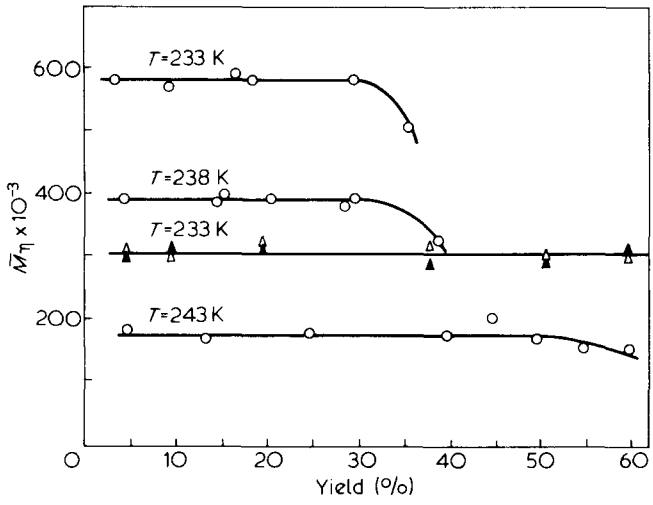


Figure 7 Copolymerization of isobutylene with isoprene in heptane and methyl chloride. The effect of conversion on the molecular mass of the copolymer. In heptane the copolymerizations were performed with the effect of light (○) at 233, 238 and 243 K, in methyl chloride they were carried out in the dark (▲) and with the effect of light (△) at 233 K. The concentrations of the monomers and initiator are the same as in *Figure 3*

of copolymerization in methyl chloride (i.e. in the dark or with the effect of light) did not affect the molecular mass or the level of unsaturation of the copolymer.

It should be stressed, in particular, that the molecular mass of the copolymer increases, in heptane solution with the effect of light, with increasing isoprene concentration up to 1.5 mol% in the injected solution. The increase in the molecular mass of the copolymer amounts to approximately twice the molecular mass of polyisobutylene alone (prepared under the same molecular mass of polyisobutylene alone (prepared under the same experimental conditions), as shown in *Figure 6*. At higher isoprene concentrations, from 1.5 to 2.5 mol%, the molecular mass of the copolymer decreases only very slowly (from the original $\bar{M}\eta$ 4000000, to 350000). A larger decrease in the molecular mass of the copolymer was recorded only at higher isoprene concentrations; however, even at 3.3 mol% isoprene the molecular mass of the copolymer is not lower than that of polyisobutylene alone.

The unsaturation of the copolymer increases linearly with increasing isoprene concentration in the injected solution (up to 2 mol%), being somewhat higher than the isoprene content (mol%) in the mixture of monomers. At higher isoprene concentrations (about 3 mol%), the unsaturation of the copolymer approximately equals the isoprene content (mol%) in the injected solution of monomers. At isoprene concentrations ~3.3 mol%, insoluble gels in amounts between 5 and 8 wt% were detected in the copolymer samples.

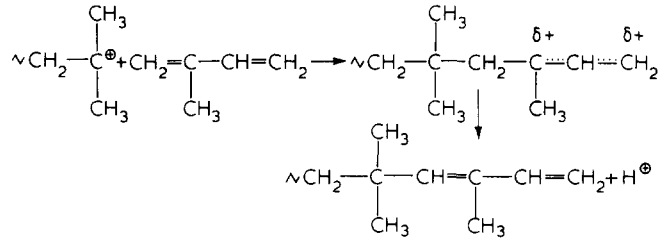
Effect of conversion: The effect of conversion on the molecular mass of the copolymer was examined in heptane solution at 233, 238 and 243K and in methyl chloride at 233K. The results are given in *Figure 7*. In methyl chloride the molecular mass of the copolymer in the investigated range of conversion (up to 60%) remained unchanged with increasing conversion and was also independent of the technique of copolymerization (i.e. in the dark or with the effect of light). In heptane solution at 243K the molecular mass of the copolymer also remained constant up to 50% conversion.

However, with proceeding polymerization the viscosity of the polymer solution increased. This fact did not allow us to maintain the isothermal character of the reaction. Hence, at a conversion higher than 50% ($T = 243$K) the molecular masses of copolymers formed were lower. Owing to the formation of copolymers possessing higher molecular masses (higher viscosity of the polymer solution) at 238 and 233K compared to those prepared at 243K, the decrease in molecular masses of the copolymer depending on conversion was recorded already after 30% conversion, as documented by *Figure 7*.

The unsaturation of copolymers obtained in heptane and methyl chloride solutions was independent of conversion. The unsaturation of copolymers prepared in heptane was ~2 mol%, while that of copolymers obtained in methyl chloride was ~1.5 mol% within the whole range of conversions under investigation.

DISCUSSION

Kennedy and Thomas have already observed a break in the log $\bar{M}\eta$ *versus* $1/T$ dependence in the polymerization of isobutylene proceeding in propane[15] and polar solvents[16] (such as ethyl chloride, vinyl chloride, mixture methyl chloride–vinyl chloride). The process was initiated with $AlCl_3$. Later, Kennedy and Squires[14] demonstrated this phenomenon using $AlCl_3$, BF_3 and $AlEtCl_2$ as initiators in the polymerization of isobutylene and copolymerization of isobutylene with isoprene in methyl chloride. The break in the log $\bar{M}\eta$ *versus* $1/T$ dependence has been observed in the temperature range from 183 to 173K both for the polymerization of isobutylene and for the copolymerization, using all the initiation systems mentioned. The authors then explained the phenomenon through the participation of the solvent and monomers in the mechanism of chain transfer reactions. At high temperatures (>183K), the chain transfer involving the solvent predominantes compared with lower temperatures (<173K), when the chain transfer to monomer prevails, while in the copolymerization at low temperatures the chain transfer and or termination involving isoprene predominantes rather than the monomer transfer reaction. Isoprene is a powerful chain transfer agent which affects the kinetic chain length by the following reactions[14]:



The transfer to solvent has been demonstrated by using C^{14}-methyl chloride and the detection of C^{14} in the polymer[17].

It cannot be decided whether, in our case also, transfer to methyl chloride in the polymerization of isobutylene with VCl_4 already decreases at 195K and the transfer to isobutylene prevails. Alternatively, however, it can be assumed that diffusion processes become operative to a considerable extent, especially when the polyisobutylene of the molecular mass ($\bar{M}\eta$) ~ 5×10^6 precipitates from methyl chloride during the polymerization. Kennedy's explanation of the predominant role of the chain transfer

involving isoprene can then be applied also to our case in the copolymerization of isobutylene with isoprene in heptane solution at temperatures below the observed break in the log $\bar{M}\eta$ *versus* $1/T$ dependence.

We cannot offer any explanation for the finding that, in the copolymerization in heptane solution with the effect of light, the molecular mass of the copolymer increases to twice its original value compared with isobutylene alone after the addition of isoprene (~ up to 1.5 mol%, *Figure 6*). For photopolymerization of isobutylene with VCl_4 in nonpolar solvent, we have suggested[7] a radical-cationic mechanism of initiation, which probably holds also for the polymerization or copolymerizations carried out in methyl chloride in the dark[8] (polymerizations do not proceed in the presence of oxygen). Initiation then probably proceeds according to the scheme:

$$M + VCl_4 \rightleftharpoons M.VCl_4 \text{ (charge-transfer complex)}$$

$$M.VCl_4 \xrightarrow{h\nu} M^{+\cdot} \; . \; VCl_4^{-\cdot} \text{ (nonpolar medium)}$$

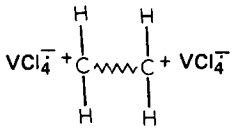
$$M.VCl_4 \xrightarrow{\text{dark}} M^{+\cdot} + VCl_4^{-\cdot} \text{ (polar medium)}$$

Following the fast recombination of radical-cations of the monomer, a carbodication is formed:

The chain propagation occurs independently at both ends of the carbodication:

$$^{+}M - M^{+} \xrightarrow{2M} {}^{+}M - M - M - M^{+} \xrightarrow{n\bar{M}} \text{Polymer}$$

It is probable that the gegenion (VCl_4^-) which is situated close to the propagating carbodication



impedes chain transfer with monomer or with methyl chloride. Owing to the decrease of transfer reactions, and perhaps also to the existence of the propagating carbodication, it is possible to explain the high molecular masses of polyisobutylene and of the copolymer of isobutylene with isoprene obtained VCl_4.

It has been reported that a small quantity of diene, and especially of isoprene, powerfully reduces the molecular mass of the copolymer compared with polyisobutylene alone. Thus, Anosov and Korotkov[18] report that the addition of 0.01 mol l^{-1} isoprene to isobutylene (polymerization with BF_3 as initiator in liquid ethylene or in the mixture ethylene–ethyl chloride) reduced the molecular mass of polyisobutylene ($\bar{M}\eta = 5.0\text{–}5.5 \times 10^6$) to $\sim 0.25 \times 10^6$. The decrease in the degree of polymerization by approximately one half after the addition of isoprene in the polymerization of isobutylene has also been described by Kennedy and Squires[14] with BF_3. $AlCl_3$ and $EtAlCl_2$. In our case, however, the molecular mass of copolymers obtained by the copolymerization of isobutylene with isoprene in heptane solution with the effect of light is higher than that of polyisobutylene alone. After the addition of isoprene up to 1.5 mol %, the molecular mass of the copolymer is doubled compared with polyisobutylene obtained under the same experimental conditions. An increase in the molecular mass of the copolymer up to as much as twice the molecular mass of polyisobutylene prepared under the same experimental conditions was also observed when butadiene had been added to isobutylene in the copolymerization in the presence of VCl_4 with the effect of visible light. Thus, in the photochemical copolymerization of isobutylene with butadiene-1,3 in the absence of an auxiliary solvent[19] at 233K with the 1,3 butadiene content from 1 to 15 wt% in a mixture of monomers, a copolymer having a molecular mass ($\bar{M}\eta$) 500 000 ($\pm$ 50 000) was formed, the conversion was 50–70% ($[VCl_4] = 2.7 \times 10^{-3}$ mol l^{-1}, unsaturation was lower by approximately one order of magnitude than the content wt% of butadiene-1,3 in the injected mixture or monomers, i.e. within the range from 0.1 to 1.5 mol%). Polyisobutylene formed under the same experimental conditions has a molecular mass ($\bar{M}\eta$) ~ 220 000 ($\pm$ 30 000). In particular, the fact may be stressed that the polymerization and copolymerization with the effect of light could be affected favourably by adding certain 'activators' not typical of cationic polymerizations, i.e. with alkali metals and their hydrides[20]. Activators accelerated photochemical polymerizations or copolymerizations and enabled the VCl_4 concentration to be reduced.

CONCLUSION

In the polymerization of isobutylene with the effect of light in the presence of VCl_4 in heptane, the addition of isoprene did not lead to any decrease in the molecular mass of the copolymer compared with polyisobutylene alone prepared under the same experimental conditions. On the contrary, the molecular mass of the copolymer was twice as high as the molecular mass of polyisobutylene. This finding is at variance with the results obtained with the known cationic initiators $AlCl_3$[14], $AlEtCl_2$[14], BF_3[14,18], where isoprene caused a powerful decrease in the molecular mass.

We believe that initiation in the photochemical copolymerization of isobutylene with isoprene in heptane proceeds via a completely different mechanism than the protonic one with $AlCl_3$, $AlEtCl_2$, BF_3 as initiators, thus confirming the radical-cationic mechanism of initiation described earlier for the photochemical copolymerization of isobutylene with isoprene[9].

In both polymerization and copolymerization, polyisobutylenes and polyisobutylene-isoprenes (butyl rubbers) having high molecular masses are formed at relatively high temperatures (from 238 to 233K) and VCl_4 appeared to be a very effective catalyst. The process of preparation of polyisobutylenes and its copolymers with isoprene in the presence of VCl_4 indicates a route for industrial application.

REFERENCES

1 Chmelir, M. and Marek, M. *J. Polym. Sci.* 1968, **C22**, 177
2 Chmelir, M. and Marek, M. *Collect. Czech. Chem. Commun.* 1967, **32**, 3047
3 Lopour, P. and Marek, M. *Makromol. Chem.* 1970, **134**, 23
4 Kennedy, J. P. 'Polymer Chemistry of Synthetic Elastomers, Part 1', Interscience, New York, 1968, p 295

5 Marek, M. and Toman, L. 'Int. Symp. on Macromolecules, Preprint 1 97', Helsinky 1972; *J. Polym. Sci., Polym. Symp.* 1973, **42**, 339

6 Toman, L., Marek, M. and Jokl, J. *J. Polym. Sci., Part A* 1974, **12**, 1897

7 Marek, M., Toman, L. and Pilar, J. *J. Polym. Sci., Polym. Chem. Edn.* 1975, **13**, 1565

8 Toman, L. and Marek, M. *J. Macromol. Sci. Chem.* 1981, **A15(8)**, 1533

9 Toman, L., Pilar, J., Spevácek, J. and Marek, M. *J. Polym. Sci., Polym. Chem. Edn.* 1978, **16**, 2759

10 Spevácek, J., Toman, L. and Marek, M. *J. Macromol. Sci. Chem.* 1981, **A16(3)**, 645

11 Kincannon, C. B. and Manning, E. *Ind. Eng. Chem.* 1955, **47**, 149

12 Toman, L., Safarík, B. and Marek, M. Czechoslov. Pat. 188650 (1978)

13 Toman, L. and Marek, M. *Makromol. Chem.* 1976, **177**, 3325

14 Kennedy, J. P. and Squires, R. G. *Polymer* 1965, **6**, 579

15 Kennedy, J. P. and Thomas, R. M. 'Polymerization and Polycondensation Processes', Adv. Chem. Ser. No. 34, Chap 7, A.C.S., Washington, 1962

16 Kennedy, J. P. and Thomas, R. M. *J. Polym. Sci.* 1961, **55**, 311

17 Kennedy, J. P. and Thomas, R. M. *J. Polym. Sci.* 1960, **45**, 227

18 Anosov, V. I. and Korotkov, A. A. *Vysokomol. Soedin.* 1960, **2**, 353

19 Marek, M. and Toman, L., Confer. Alkén, 1973, Mariánské Lázne, Preprint C, 131

20 Marek, M. and Toman, L., Czechoslov. Pat. 150 800, 1973; US Pat. 3 998 713 (1976)