Simulation of coupled modification reactions of polymers: 5. Formation of conjugated double bonds by substitution of 1,4-polybutadiene coupled with partial double bond shift*

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The possibility that 1,4-polybutadiene may become coloured by radical substitution coupled with partial double bond shift (allyl rearrangement) was investigated. The fraction of C atoms in the resulting conjugated systems and the length of the conjugated systems as a function of both the substitution degree and the shift probability were determined by computer simulation. The fraction of C atoms found in conjugated systems by using a model with multiple double bond shift (α,ω-reaction) was up to 0.42. The conjugated systems contained significant percentages of up to five double bonds and traces of up to 11 double bonds. This is insufficient for a marked colouring of linear chains, but sufficient if crosslinking via substitution of double bonds is considered.

(Keywords: Monte Carlo simulation; 1,4-polybutadiene; substitution; double bond shift; colour)

INTRODUCTION

The colour of technical polymers is a property relevant for practical applications. In some cases colouring is due to the presence of systems of conjugated double bonds. Substances like $X\!-\!\!(CR_1\!=\!CR_2)_{\overline{z}}\,Y$ ('π-conjugation') absorb in the visible range of the spectrum if z exceeds a minimum value dependent on the structure of the substituents X, Y, R_1 and R_2. Simple polyenes $CH_3\!-\!\!(CH\!=\!CH)_{\overline{z}}CH_3$ with $z > 5$ are coloured[1].

Radical substitution reactions of 1,4-polybutadiene, e.g. with alkylbenzenes and dicumyl peroxide as radical donor, are considered below as a possible cause for the formation of conjugated double bonds. Substitution is coupled here with partial double bond shift (allyl rearrangement)[2,3]. In preparatory investigations[2], some of the higher modified products received were yellow-brown, but there was no unambiguous evidence that the colour resulted from conjugated systems in the polymer backbone. In principle, conjugated double bonds could be formed in these reactions in only a few steps, as the example of equation (1) shows ($R^{\cdot}$ = arbitrary radical). Longer systems of conjugated double bonds could be formed in the same way. Substituted conjugated double bonds could also result from a repeated reaction at the same allylic system; see equation (2).

Computer simulation (Monte Carlo calculation) seemed to be a promising method of obtaining information about this type of reaction. Simulations are standard for the investigation of polymer analogous reactions of polymers and the formation of copolymers since the work of Harwood[4], Litmanovich[5] and Klesper *et al.*[6,7], but our case differs crucially in that the polymer backbone itself is modified by the double bond shift. In addition, sites of the polymer chain which have already reacted can repeatedly take part in the reaction. We have already investigated some general characteristics of such reactions by simulation[8]. Good agreement with experimental results has been found[9].

The reaction is described by pg = polymerization degree of the starting 1,4-polybutadiene, su = number of substituents in a molecule/pg, and ag = shift probability. If a double bond shift is in principle allowed, then ag decides whether the shift takes place or not. The fraction and length of the conjugated systems and the substitution of the double bonds within these systems were determined as a function of su and ag.

REACTION MODELS

There is an almost infinite number of possible situations in reactions of the type of equations (1) and (2) (especially

$$\begin{aligned}
&-CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH- \xrightarrow{-H} -CH{=}CH{-}CH_2{-}\dot{C}H{-}CH{=}CH-\\
&\leftrightarrow -CH{=}CH{-}CH_2{-}CH{=}CH{-}\dot{C}H- \xrightarrow{+R\cdot} -CH{=}CH{-}CH_2{-}CH{=}CH{-}CHR- \xrightarrow{-H} -CH{=}CH{-}\dot{C}H{-}CH{=}CH{-}CHR-\\
&\leftrightarrow -CH{=}CH{-}CH{=}CH{-}\dot{C}H{-}CHR- \xrightarrow{+R^{\cdot}} -CH{=}CH{-}CH{=}CH{-}CHR{-}CHR- \qquad (1)
\end{aligned}$$

$$\begin{aligned}
&-CH{=}CH{-}CHR{-}CH{=}CH- \xrightarrow{-H} -CH{=}CH{-}\dot{C}R{-}CH{=}CH-\\
&\leftrightarrow -CH{=}CH{-}CR{=}CH{-}\dot{C}H- \xrightarrow{+R\cdot} -CH{=}CH{-}CR{=}CH{-}CHR- \qquad (2)
\end{aligned}$$

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if different reactivities are included) and for this reason simulation has to be limited to the simplest reaction models, corresponding to a general simulation strategy[10]. Our models ignore a possible unequal reactivity of the H atoms in $-CH_2-$ and $-CHR-$. Only one general shift probability *ag* is used for all types of double bond ($-CH{=}CH-$, $-CR{=}CH-$ or $-CH{=}CR-$, and $-CR{=}CR-$). Neighbouring group effects concerning substitution or double bond shift are ignored. Doubly allylic and singly allylic positions are not differentiated. As has been shown previously for similar investigations, these simplifications have no marked influence on the general aspects of the results[9].

Three different models are considered below. They have in common that hydrogen abstraction is only possible from groups $-CH_2-$ and $-CHR-$ adjacent to double bonds (allyl position) and double bond shift without simultaneous substitution is not allowed. The models differ in their treatment of the conjugated double bonds.

Model I can be called the 'standard model'. Only one double bond is shifted in each reaction step. The length of a conjugated system can be increased, e.g.

$$-CH{=}CH-CH_2-CH{=}CH- \rightarrow$$

$$-CH{=}CH-CH{=}CH-CHR-$$

or decreased, e.g.

$$-CH{=}CH-CH{=}CH-CH_2- \rightarrow$$

$$-CH{=}CH-CHR-CH{=}CH-$$

A characteristic feature is that only three C atoms of the chain are involved in a reaction step.

In model II, the 'conjugation-protected' model, conjugated systems do not participate in shift reactions, e.g.

$$-CH{=}CH-CH{=}CH-CH_2- \nrightarrow$$

$$-CH{=}CH-CHR-CH{=}CH-$$

The number of double bonds in the conjugated system can only be increased, not decreased.

Model III, the 'multiple shift' model, is characterized by a shift of the whole conjugated system, e.g.

$$-CH{=}CH-CH{=}CH-CH_2- \rightarrow$$

$$-CHR-CH{=}CH-CH{=}CH-$$

or

$$-CR{=}CR-CR{=}CR-CR{=}CH-CH_2- \rightarrow$$

$$-CR_2-CR{=}CR-CR{=}CR-CH{=}CH-$$

The length of the shifting system is not limited in this model (α,ω-reaction) and the reaction could include, for example, half the macromolecule. Conjugated systems once formed are protected from reduction in size as in model II.

The quantity sh = number of shift events in a molecule/pg, which has been used in previous investigations[8], allows a further distinction between the three models: $sh/su = ag$ in model I, $sh/su < ag$ in model II and $sh/su > ag$ in model III.

SIMULATION

A general program for computer simulation of this type of reaction published recently[11] was modified for this investigation by using a variant of the 'decreasing-table technique'[12]. The implementation of the above models is described elsewhere[13].

All decisions in the program are made by random numbers. The possible substitution sites $-CH_2-$ and $-CHR-$ are selected with an integer random number between one and the length of the decreasing table. A comparison of the preset value of *ag* with a random number between 0 and 1.0 decides whether a double bond shift takes place. A comparison of 0.5 with another random number between 0 and 1.0 decides the direction of the double bond shift in the case of propanediylidene units.

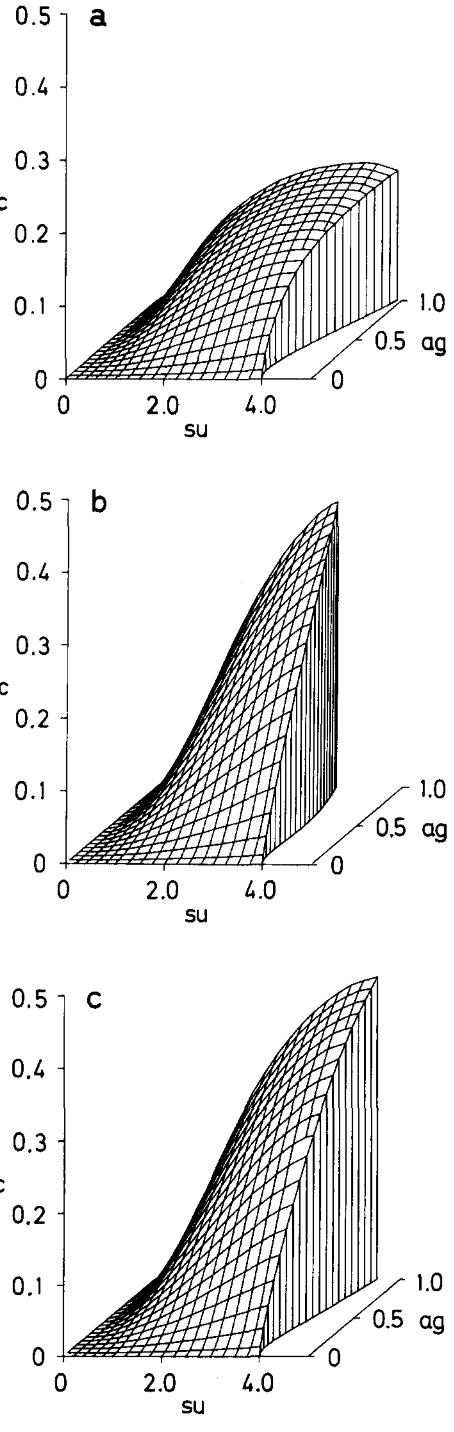


Figure 1 Fraction x_C of C atoms in conjugated double bonds as a function of *su* and *ag*: (a) model I; (b) model II; (c) model III

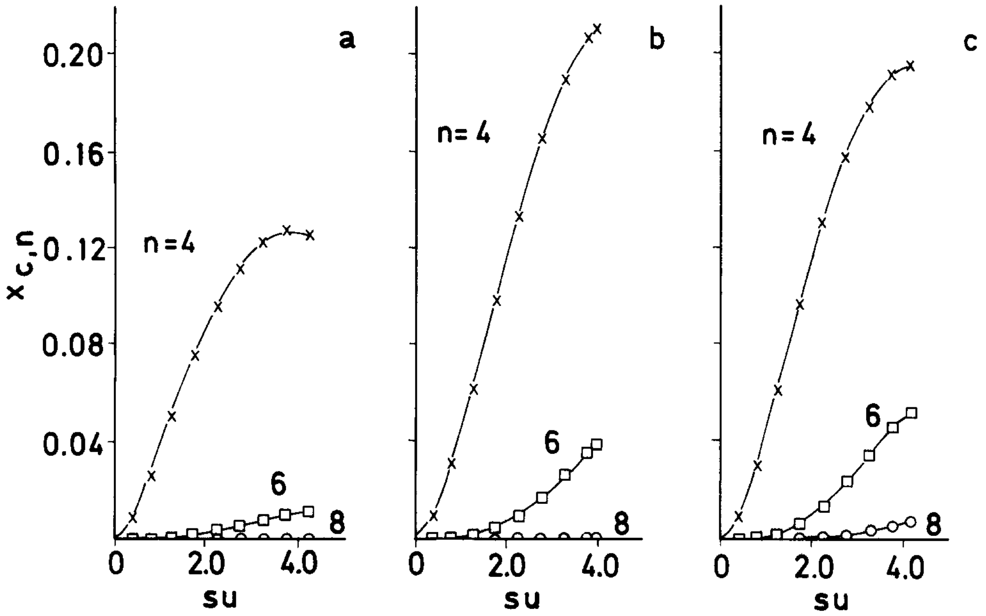


Figure 2 Fraction $x_{C,n}$ of C atoms in conjugated systems of different length n as a function of su for $ag = 0.5$: (a) model I; (b) model II; (c) model III

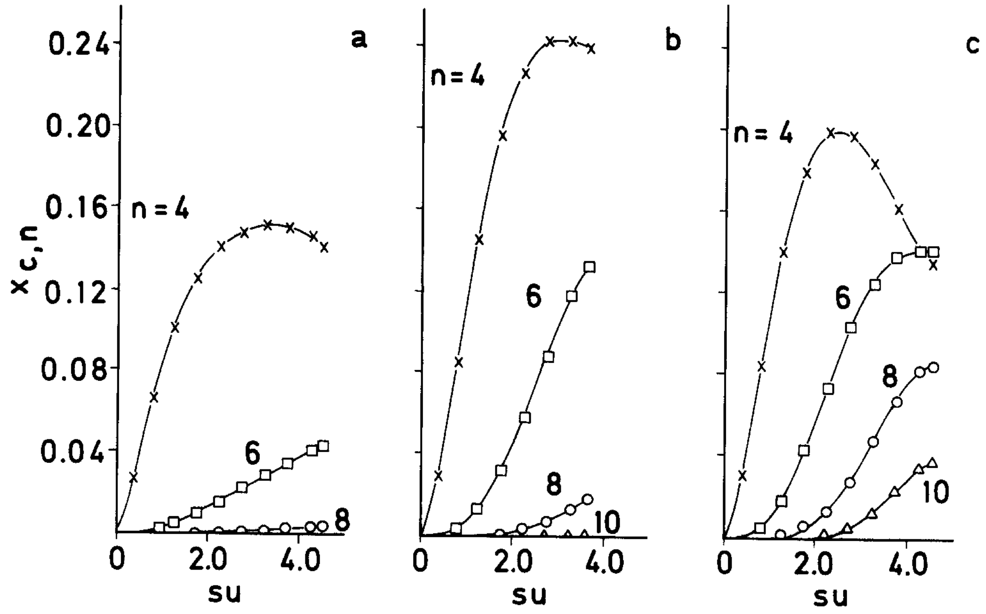


Figure 3 Fraction $x_{C,n}$ of C atoms in conjugated systems of different length n as a function of su for $ag = 1.0$: (a) model I; (b) model II; (c) model III

RESULTS AND DISCUSSION

Calculations were carried out for a collection of 100 macromolecules with $pg = 3000$. The 100 repeat runs in the simulation were sufficient to reduce statistical noise[14].

Figure 1 shows the fractions x_C of C atoms in conjugated double bonds for models I–III as a function of su and ag in three-dimensional histograms. The reaction comes to a standstill at a certain value of su dependent on the reaction model and ag. For $ag = 0.5$, these values of su are 4.25 (model I), 3.93 (model II) and 4.15 (model III). For $ag = 1.0$ the corresponding values are 4.92 (model I), 3.64 (model II) and 4.53 (model III). It is interesting that the maximum values for models I and III are at $ag = 1.0$, but that for model II is at $ag \approx 0.5$. The assumptions in the models also have a great influence on x_C. A value $x_C = 0.50$ would mean that all double bonds of the polymer were in conjugated systems. For $ag = 0.5$, the values of x_C at the maximum of su are 0.136 (model I), 0.250 (model II) and 0.254 (model III). For $ag = 1.0$, the corresponding values are 0.178 (model I), 0.391 (model II) and 0.418 (model III). Only for model I is the maximum value $x_C = 0.189$ not found at the maximum of su and ag. Conjugated systems are not significant at all if both su and ag are < 0.2.

The fraction of C atoms $x_{C,n}$ in conjugated systems with n C atoms is shown for $ag = 0.5$ in *Figure 2* and for $ag = 1.0$ in *Figure 3*. Conjugated systems with $n = 4$ (two double bonds) are dominant in all cases except model III at high values of su and with $ag = 1.0$. The curves for $n = 4$ have maxima (all three models for $ag = 1.0$ and also model I for $ag = 0.5$). All curves have turning points. The multiple shift in model III and $ag = 1.0$ favour the formation of conjugated systems with more C atoms, but

Table 1 Substitution coupled with partial double bond shift in 1,4-polybutadiene: examples of long units[a]

	Model		
ag	I	II	III
0.5	54333113345	54333133345	243334114344442
	24434344435	23431133345	24444434144442
	53433333345	53331333345	54333311443345
1.0	543333133433445	54444443344345	54334343343333344344442
	543431333433445	54333311333345	5444444443444113333442
	54333313343345	54444441334345	5444444343113434343445

[a] Abbreviations: 1, $-CH_2-$; 2, $-CH{=}$ or $=CH-$, 3, $-CHR-$; 4, $-CR_2-$; 5, $-CR{=}$ or $=CR-$. The units occurred only once for all values of *su* (100 repeat runs for each value of *su*)

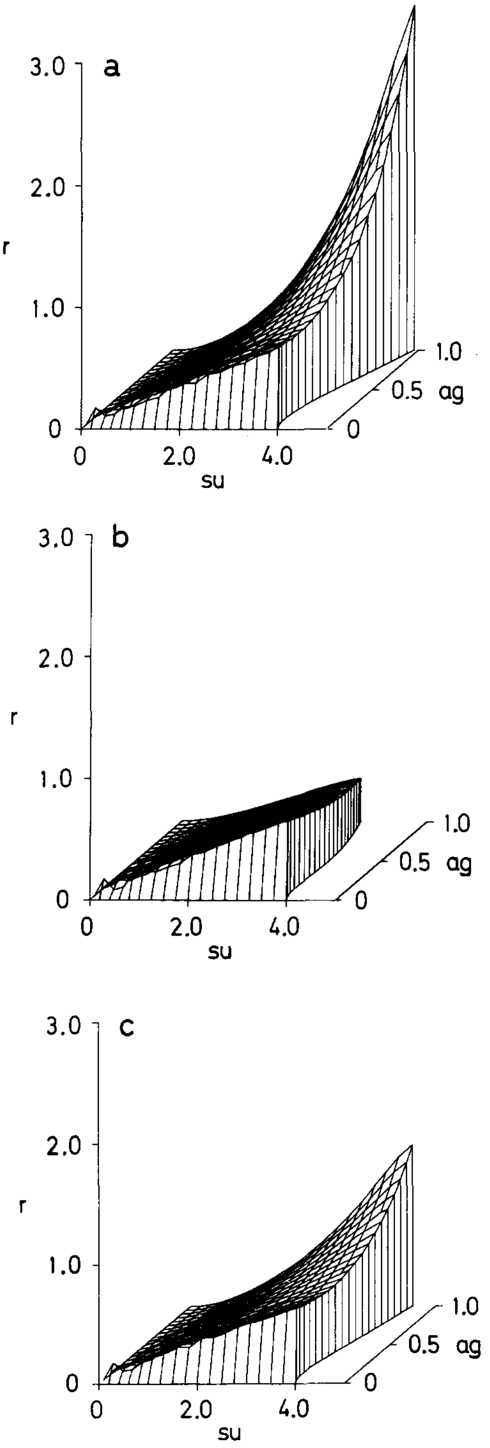


Figure 4 Ratio *r* of substituted double bonds to unsubstituted double bonds as a function of *su* and *ag*: (a) model I; (b) model II; (c) model III

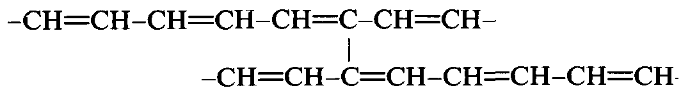
conjugated systems occurring to a reasonable extent have here a value of $n < 12$. For $ag = 0.5$, the maximum values of *n* found in traces are 8 (model I), 10 (model II) and 12 (model III). For $ag = 1.0$, the corresponding values are 12 (model I), 12 (model II) and 22 (model III). It can be seen that the results for $ag = 0.5$ and 1.0 are different, especially for model III.

The formation of relatively long units (considered from one double bond to the next) is the consequence of this formation of conjugated systems. Examples of the largest units found in traces are shown in *Table 1*. Units with up to 24 C atoms in the chain are obtained with model III and $ag = 1.0$; $-CH_2-$ groups have remained near the centre in these long units.

Figure 4 shows the ratio *r* of substituted double bonds to unsubstituted double bonds in the conjugated systems without the delimiting $-CH{=}$, $=CH-$, $-CR{=}$ or $=CR-$ as a function of *su* and *ag* for models I–III. Fluctuations of *r* are perceptible for low values of *ag*. The cause is the low absolute number of double bonds in conjugated systems in the given conditions for all models, so that mean values of *r* have a relatively high standard deviation. Substituted C atoms $-CR{=}$ or $=CR-$ become dominant in conjugated systems for models I and III at high values of *su* and *ag*. For model I, *r* has a maximum of ≈2.8 and, for model III, a maximum of ≈1.3. For model II, $-CR{=}$ or $=CR-$ groups are less probable for all values of *su* and *ag*.

CONCLUSIONS

As shown above, most of the double bonds of 1,4-polybutadiene are transferred to conjugated systems by substitution coupled with double bond shift under appropriate reaction conditions (high values of *su* and *ag*, multiple shift model III). But most of the conjugated systems formed in the polymer chains are not long enough to colour the polybutadiene; conjugated systems with six or more double bonds necessary for colour are formed only in traces. However, coloured products will result even with rather short conjugated systems in a single chain when crosslinking via $-CR{=}$ or $=CR-$ (occurring with sufficient frequency in model I and III) takes place. If the radicals $R^{\cdot}$, recombining with the polymer radicals in reactions of the type of equation (1) and (2), are other polymer radicals, then larger conjugated systems consisting of more than one polymer chain can be expected in the products, e.g.



$$\begin{array}{l} -CH{=}CH{-}CH{=}CH{-}CH{=}C{-}CH{=}CH- \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad -CH{=}CH{-}C{=}CH{-}CH{=}CH{-}CH{=}CH- \end{array}$$

Thus the conjugated systems of 3–5 double bonds in single chains found in simulation (see *Figures 2* and *3*) seem to be sufficient to colour the polymer if they are combined by crosslinking.

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