DOI: 10.1002/masy.201151003

Peculiarities of the Anionic Copolymerization of Styrene and Dienes in Non-Polar Solvents with Li^+ as Counter-ion mvb

Marcel Van Beylen,[*1] *Hideo Morita*[2]

Summary: The anionic copolymerization of styrene and butadiene in hydrocarbon solvents initiated by lithium alkyls was first studied by Korotkov, who reported that the polymerization starts slowly and initially consumes butadiene. On exhaustion of this monomer, the reaction speeds up and then styrene polymerizes rapidly. This peculiar behaviour, which was originally explained by Korotkov by treating the monomers as solvents, butadiene being a preferential solvent for the Li^+ cation, was later accounted for by considering the cross-over reactions. In this paper an in dept further explanation is given by admitting that the polymerization reactions occur through coordination of the Li^+ cation by the monomer followed by insertion of the monomer into the polymer chain. A preliminary MOPAC 93 (PM3) calculation seems to confirm this interpretation.

The anionic copolymerization of styrene and butadiene in hydrocarbon solvents by lithium alkyls, as first reported by Korotkov[1] is rather unexpected. Indeed although styrene homopolymerizes faster than butadiene, the copolymeriza bymerization of a mixture of these monomers starts slowly and initially only butadiene is consumed. After this monomer becomes depleted, the reaction speeds up and styrene then polymerizes rapidly. This is illustrated in Figure 1.

Korotkov explained this unusual behaviour by trating the monomers as solvents of the growing species.

Butadiene, being a preferential solvent was expected to be presentalmost exclusively around the Li^+ cation of the growing chain-end, excluding thereby the more poorly solvating styrene from the reaction center. Therefore butadiene plymerizes preferentially, albeit slowly, followed after its consumption by the rapid polymerization of the more reactive styrene.

O'Driscoll and Kuntz[2] explained the unusual phenomenon by pointing out, that, although styene (S) homopolymerizester than butadiene (B) the cross-over rate constant of polysryryllihium (PStLi) with butadiene is much larger than the homopropagation rate constant for PStLi, whereas the rate constant for the addition of styrene to polybutadienyllithium (PBdLi) is very small. Moreover as the homopropagation of styrene is faster than that of butadiene, almost all active centers in the beginning of the reaction are PBdLi centers, since addition of styrene will be rapidly followed by addition of butadiene and the PBdLi will then slowly homopolymerize, since the cross-over into PStLI is very slow. Only after the consumption of butadiene, styrene starts to homopolymerize, causing an increase of rate.

The different reactions taking place can be represented ad follows:

$$
\begin{aligned}
(PSty_nLi)_2 \overset{K_s}{\longleftrightarrow} 2PSty_nLi \quad & PSty_nLi + Sty \xrightarrow{k_{SS}} PSty_{n+1}Li \\
& PSty_nLi + Bd \xrightarrow{k_{SB}} PSty_nBdLi \\
(PBd_nLi)_4 \overset{K_B}{\longleftrightarrow} 4PBd_nLi \quad & PBd_nLi + Sty \xrightarrow{k_{BS}} PBd_nStyLi \\
& PBd_nLi + Bd \xrightarrow{k_{SB}} PBd_{n+1}Li
\end{aligned}
$$

In fact Figure 1 reflects the effects of the apparent rate constants which actually include the dissociation constants

---

[1] University of Leuven, B-3001 Heverlee, BELGIUM
E-mail: marcel.vanbeylen@chem.kuleuven.be

[2] 50-5 Torigaoka, Totsukaku, Yokohama, 44-0001 Japan

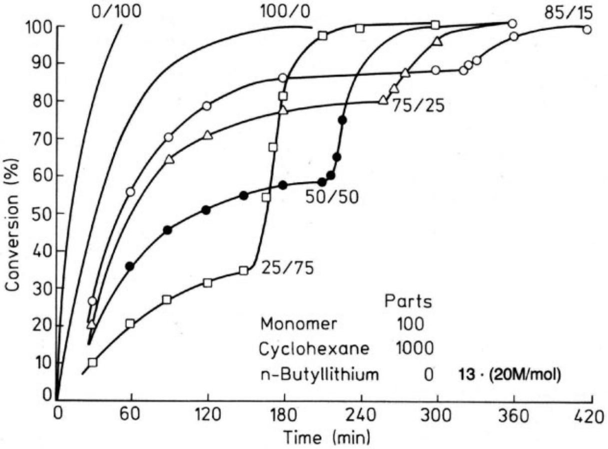

Figure 1.
Copolymerization of butadiene and styrene by *n*-BuLi in cyclohexane. Note the initial polymerization of butadiene followed by the much faster styrene polymerization.

(K_i) for the chain ends, this is k'_{ij} (apparent) $= k_{ij}\ K_i^{1/n}$ in which k_{ij} is the actual propagation constant and n is the degree of association of the chain ends. The shape of Figure 1 should then require:

$$k'_{SB} >> k'_{SS} > k'_{BB} > k'_{BS}$$

It is therefore not possible to say a priori whether the differences are due to the greatere intrinsic reactivity of the free ion pair or to the higher dissociation of the aggregate. However, as shown later by Worsfold,[5] who studied not only the homopolymerization rates of both monomers but also the rates of the cross-over reactions of each individual chain end whith the opposite monomer in the absence of the other, where the association effects are cancelled, in the case of the the copolymerization of isoprene and styrene (see further) it was seen that $k_{I\ S} >> k_{SS}$ and $k_{II} > k_{IS}$.

Thus in the case of styrene and butadiene $k'_{SB} >> k'_{BS}$ and $k'_{BB} >> k'_{BS}$ and $k'_{SS} >> k'_{BB}$ where $k'_{ij} = k_{ij}K_i^{1/n}$ (where n = 2 for PStLi and 4 for PBdLi).

This was verified by Ells and Morton[3] and by Johnson and Worsfold,[4] who determined the respective rate constants. As mentioned above Worsfold[5] also investigated the closely related copolymerization of styrene and isoprene and determined the above given association numbers.

The question of why dienes add so much faster to PStLi than styrene (in other words why $k'_{SB} >> k'_{SS}$ or $k_{SB} >> k_{SS}$)[6] was attributed by Szwarc and Van Beylen[7] to the fact that Li^+ ion coordination by monomers takes place prior to insertion of the monomer in the polymer chain in hydrocarbons. This coordination seems to facilitate the reaction making the lithium salt more reactive and butadiene is certainly more strongly coordinating than styrene.

The proposed reaction scheme is as follows:

$$P_n^- Li^+ + \text{Monomer} <==> [P_n^- Li^+, M]^-$$
$$\rightarrow P_{n+1} - Li^+$$

i.e reversible complex formation of monomer with living polymer in which the monomer becomes coordinated to the living end of the polymer followed by a unimolecular rearrangement during which the monomer is incorporated into the polymer chain.

This idea is corroborated by the findings of Jurgen Hofmans and M. Van Beylen [8–10] that $PBdLi^+$ in C_6H_{12} to which durene (tetramethylbenzene), a π-complexing agent,

Table 1.
Results of MOPAC 93 P: calculations

	ΔH (Kcal/mol)	Ea (Kcal/mol)	Apparent activation energy of total reaction Ea app (Kcal/mol) = ΔH + Ea
BdLi-Bd	−21.7	+18	−3.7
BdLi-Sty	−17.1	+22.3	+5.2
StyLi-Sty	−17.4	+20	+2.6
StyLi-Bd	−22.4	+18.3	−4.1

was added will not add styrene, because the stronger coordinating durene will prevent the coordination of styrene, whereas it does add butadiene, which is a stronger coordinating agent than both durene and styrene.

! However a second factor which seems important is the reactivity of the ion-pair to which the monomer is going to be added after its coordination.

This is seen because styrene which will not add to PBut-Li^+ complexed with durene is found to add to PStLi complexed with durene (Guoming Wang, A. Yakimanski and M. Van Beylen).[9,10]

Two factors seem therefore important for reaction of the monomer with a chain-end with Li^+ as counterion, viz:

- the coordinating power of the monomer for the Li^+ -cation.
- Reactivity of the P^-Li^+ ion-pair.

Therefore in the copolymerization of butadiene and styrene with alkylLi initiator in non-polar solvents: two factors influence the reaction:

- the coordinating power of monomer: butadiene or styrene
- the reactivity of the chain-end: PBd-Li^+ or PSt-Li^+

On this basis the following 4 reactions in the copolymerization were considered.

On this system Hideo Morita (Theoretical Chemist,Yokohama, Japan carried out some theoretical MOPAC 93 (PM3) calculations.

The results of these calculations are shown in Table 1

From this table we concluded for

$$-\Delta H: \text{BdLi-}\underline{\text{Bdt}} \leftrightarrow \text{BdLi-}\underline{\text{Sty}}$$
$$21.7 \qquad 17.1$$
$$-\Delta H: \text{StyLi-}\underline{\text{But}} \leftrightarrow \text{StyLi-}\underline{\text{Sty}}$$
$$22.4 \qquad 17.4$$

which indicates that butadiene is a better π-complexing agent than styrene for the same ion-pair. This can be shown more clearly in the following way.

$$\text{BdLi} + \text{But} \leftrightarrow (\text{BdLi})(\text{Bd}) \quad \Delta H = -21.7 \tag{1}$$

$$\text{BdLi} + \text{Sty} \leftrightarrow (\text{BdLi})(\text{Sty}) \quad \Delta H = -17.1 \tag{2}$$

Influence ΔH

$$(1) - (2): \text{Bd-Sty} \leftrightarrow (\text{BdLi})(\text{Bd}) - (\text{BdLi})(\text{Sty}) \quad \Delta\Delta H = -4.6 \tag{3}$$

or

$$(\text{BdLi})(\text{Sty}) + \text{Bd} \leftrightarrow (\text{BdLi})(\text{Bd}) + \text{Sty} \quad \Delta\Delta H = -4.6 \tag{4}$$

Equation 4 is the conclusion.

We can also obtain ΔΔH of Equation 4 by substituting the calculated values in the

$$PBd_nLi^+ + Bd \overset{K/\Delta H}{\longleftrightarrow} [PBd_n, Li^+, Bd] \overset{k_p/E_a}{\longrightarrow} PBd_{n+1}Li$$
$$PBd_nLi^+ + Sty \overset{K/\Delta H}{\longleftrightarrow} [PBd_n, Li^+, Sty] \overset{k_p/E_a}{\longrightarrow} PBd_nStyLi$$
$$PSty_nLi^+ + Bd \overset{K/\Delta H}{\longleftrightarrow} [PSty_n, Li^+, Bd] \overset{k_p/E_a}{\longrightarrow} PSty_nBdLi$$
$$PSty_nLi^+ + Sty \overset{K/\Delta H}{\longleftrightarrow} [PSty_n, Li^+, Sty] \overset{k_p/E_a}{\longrightarrow} PSty_{n+1}Li$$

following equation.

$$\Delta\Delta \mathrm{H} = (\mathrm{BdLi})(\mathrm{Bdt}) + \mathrm{Sty} - (\mathrm{BdLi})(\mathrm{Sty}) - \mathrm{Bd} = 36.1 + 39.1 - 48.1 - 31.7 = -4.6$$

In the same way, Equation 5 is obtained:

$$\Delta\Delta \mathrm{H}(\mathrm{StyLi})(\mathrm{Bd}) + \mathrm{Sty} \leftrightarrow (\mathrm{StyLi})(\mathrm{Sty}) + \mathrm{Bd}\,\Delta\Delta \mathrm{H} = 5.0 \qquad (5)$$

Influence of Ea:

$$\mathrm{Ea}: \underset{22.3}{\underline{\mathrm{BdLi}}\text{-}\mathrm{Sty}} > \underset{20}{\underline{\mathrm{StyLi\text{-}Sty}}}$$

indicates that PStyLi is more reactive than PBdLi for the same complexing agent Sty.

$$\mathrm{Ea}: \underset{18}{\mathrm{BdLi} - \mathrm{Bd}} \le \underset{18.3}{\mathrm{StyLi} - \mathrm{Bd}}$$

The latter gives the opposite for Ea than for BdLi-Sty and StyLi-Sty but is the latter difference significant? It could also mean that when the complexing agent is strong like butadiene the difference due to the anion is less outspoken.

Comment:

Ea of BdLi-But should be regarded to be in the same order of magnitude as that of StyLi-Bd since the difference is very small. To answer the latter question definitely, more precise methods of calculation such as HF or DFT will be needed.

Additional comment:

Comparing the Eaapp's of BdLi-But and BdtLi-Sty we can conclude that $k'_{BB} >> k'_{BS}$. Also the result that $k'_{SB} >> k'_{SS}$ is obtained. However, for comparison of different Li- species such as BdLi and StyLi, heat of dissociation has to be taken into account as now these apparent activation energies pertain of course to the non-aggregated species PBdLi and PStyLi.

So far the overall activation energy one should also take into account the ΔH for dissociation which we also do not know exactly.

However assuming some approximate value of ΔHdiss for $(\mathrm{BdLi})_4$ equal to e.g. 123 kcal/mol and about 45 Kcal/mol for (PStyLi)2 into non aggregated species.

Then the overall activation energies including the dissociations energy for the aggregated species become for:

k'_{BB}: ΔHdiss/4 + (−3.7) = 30.8– 3.7 = 27.1 kcal/mol
k'_{BS}: 30.8 + 5.2 = 36.0 kcal/mol
k'_{SS} : Δdiss/2 + 2.5 = 22.5 + 2.5 = 25 kcal/mol
k'_{SB} : 22.5 − 4.1 = 18.4 kcal/mol

which is in agreement with:

$$\begin{array}{cccccc} k'_{SB} >> & k'_{BS} & k'_{BB} >> & k'_{BS} & k'_{SS} \ge & k'_{BB} \\ 18.4 & 36.0 & 27.1 & 36.0 & 25.0 & 27.1 \end{array}$$

(see remark above)

More quantitative experimental results were reported by D.J. Worsfold for the anionic copolymerization of styrene with the more experimentally treatable isoprene.[5] It was found that

$$\underset{5.13\cdot 10^{-1}\,\mathrm{M}^{1/2}}{k'_{SI}} >> \underset{2.29\cdot 10^{-2}\,\mathrm{M}^{1/2}}{k'_{SS}} > \underset{3.41\cdot 10^{-3}\,\mathrm{M}^{1/4}}{k'_{II}} > \underset{2.37\cdot 10^{-4}\,\mathrm{M}^{1/4}}{k'_{IS}}$$

These apparent rate constants given in $\sec^{-1}$ include the dissociation constant K; for the chain ends, that is, as mentioned above $k'_{ij}(\mathrm{apparent}) = k_{ij}\,Ki1/n$ in which k_{ij} is the actual propagation constant and n is the degree of association (n = 2 for PStyLi and n = 4 for $\mathrm{PIspr^{-}Li^{+}}$ as determined by Worsfold.

Conclusion

This would then mean that if the π-complexing monomer is strongly π-complexing, ΔH of complexation is the main determining factor.If the monomer is less strongly π-complexing like e.g. styrene, Ea of the insertion of the monomer is the main determining factor.

It is therefore completely understandable that although styrene homopolymerizes faster than butadiene, the rate of cross-over from polystyryllithium to polybutadienyllithium is much faster than the homopropagation of styrene and the reaction starts slowly and is due to addition of butadiene to PBdLi. Should any PStLi nevertheless be formed by addition of a styrene molecule (and addition of styrene to PBdLi is slow) it will immediately be converted again to PBdLi by the very rapid addition of butadiene to PStyLi. It is only when butadiene becomes depleted that styrene gets a chance to react and then the reaction switches over to the relatively rapid homopolymerization of styrene and the over-all rate therefore increases.

Additional remarks:

- The non-aggregated PStyLi ion-pair is a less tight ion-pair (as indicated by its greater ionisation constant and higher amount of solvent separation in polar solvents) than Pbutadienyl (PBdLi) and Pisoprenyl ($PIspr^{-}Li^{+}$) ion pairs.
- Whether in an intermediately formed monomer coordinated ion-pair or in a preliminary step of a transition state, the coordination of the Li^{+}-ion with the monomer preceeding the insertion of monomers, may increase the reactivity (much as a solvent in solvent-separated ion-pairs) by increasing the $C\ldots Li^{+}$ formed as in solvent separated ion-pairs and facilitating monomer insertion into this $C\ldots .Li^{+}$) of the ion-pair. Therefore it is not surprising to find negative Ea's in the calculations. This may be compared to Korotkov's solvent theory, whereby he treats the monomers as solvents, which may solvate preferentially and as in the case of the formation of solvent-separated pairs, negative activation energies may then well appear and not be surprising.
- Finally it should be pointed out that, although with MOPAC 93 (PM3) calculations the unusual copolymerization of butadiene and styrene is explained coherently, discussion based on more reliable calculations like DFT would be necessary and we are doing them now.

Acknowledgements: The authors would like to thank Dr. Guy Koekelberghs and Drs. Alfons Smeets for their assistance with the layout of this paper.

[1] A. A. Korotkov, *Angew. Chem.* **1958**, *70*, 85.
[2] Kf. O'Driscoll, J. Kuntz, *J. Polym. Sci.* **1962**. *61*, 19.
[3] M. Morton, F. R. Ells, *J. Polym. Sci.* **1962**, *61*, 25.
[4] A. F. Johnson, D. J. Worsfold, *Makromol. Chem.* **1965**, *85*, 273.
[5] D. J. Worsfold, *J. Polym. Sci A-1* **1967**, *5*, 2783.
[6] M. Szwarc, M. Van Beylen, *Ionic polymerization and living polymers*, New York Chapman & Hall, **1993**.
[7] M. Van Beylen, S. Bywater, G. Smets, M. Szwarc, D. J. Worsfold, *Adv. Polym. Sci.* **1988**, *86*, 87.
[8] J. Hofmans, L. Maeseele, G. Wang, K. Janssens, M. Van Beylen, *Polymer*, **2003**, *44*, 4109.
[9] G. Wang, M. Van Beylen, *Polymer* **2003**, *44*, 6205.
[10] A. Yakimansky, G. Wang, K. Janssens, M. Van Beylen, *Polymer*, **2003**, *44*, 6457.
[11] J. Hofmans, M. Van Beylen, *Polymer* **2005**, *46*, 303.
[12] H. Morita, private communication.
[13] S. Bywater, *Prog. Polym. Sci.* **1994**, *19*, 287.