Anionic copolymerization of butadiene and styryl-terminated polystyrene macromonomers

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Summary

For the preparation of graft copolymers of the type poly (butadiene-g-styrene), possibilities were investigated both of obtaining a "living" anionic copolymerization of butadiene and styryl-terminated polystyrene macromonomers and of assessing the necessary analytical prerequisites for determining the conversion. The course of this copolymerization can be observed by combining gravimetry with SEC. With the initiator system sodium tert-butoxide /n-butyl lithium there are only a few deviations from the statistically ideal course of copolymeri-zation and the macromonomer is almost completely incorporated into the copolymer.

Introduction

Block copolymers-consisting of central elastomer blocks and outer thermoplastic blocks exhibit an advantageous combi-nation of good mechanical and favourable processing properties. Three-or star-block copolymers of this kind have been known for many years as thermo-elastoplastics and they are manufactured and applied in practice /1/. Also graft polymers of the type poly(butadiene-g-styrene) where the elastomer backbone chain is connected to thermoplastic grafts show thermo-elastoplastic qualities. In the literature mainly methods of radical, anionic and cationic grafting or polymer analogous reactions with reactive polymers are suggested for their preparation /2/. All these methods have advantages and disadvantages and mainly result in less well-defined products with partial cross linking and varying amounts of unbound polystyrene. Only in a few cases is it possible to definitely determine the molecular mass and MWD of grafts.

Copolymers with definite graft length can, among other things, be successfully synthesized by copolymerization with macromonomers. However, according to the results of KENNEDY /3/ and also to our own, the radical copolymerization of butadiene with polystyrene macromonomers does not lead to the formation of the desired graft polymers. For this reason we applied the anionic copolymerization method. This paper is intended to be a report on the synthesis of macromonomers, on the analytical problems of copolymerization with butadiene and it also presents the first results of successful anionic copolymerization of butadiene and polystyrene macromonomers.

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Experimental

The preparation of the styryl-terminated polystyrene macro-
monomers and their anionic copolymerization with butadiene was
carried out in a vacuum apparatus made of glass by employing
the condensation and syringe technique. Experiments were carried
out in purified argon to exlude oxygen and moisture.

Synthesis of polystyrene macromonomers:

The synthesis of styryl-terminated macromonomers was carried
out according to a proposal made by ASAMI /4/. Polystyryl lithium
was synthesized by the polymerization of styrene with freshly
preparad sec-butyl lithium in benzene and was coupled with
p-vinyl benzyl chloride (p-VBC) in a solvent-mixture of benzene
and THF. The required p-VBC was synthesized as prescribed by
KONDO /5/ and used in the coupling process in a ten-fold excess.
After precipitating macromonomers in an excess amount of metha-
nol, reprecipitation was carried out several times in order to
further purification. The powdery products were vacuum-dried.

Copolymerization of polystyrene macromonomers with butadiene:

After careful purification of the macromonomers from distur-
bing contamination they were applied to the ionic copolymeri-
zation with butadiene in cyclohexane. Butadiene was destabili-
zed, dried over a molecular sieve (A 4) and condensed on a
sodium mirror immediately before use. The polymeriziation was
started by an initiator suspension consisting of the reaction
product of n-butyl lithium and sodium tert-butanolate (1 : 1).
At the beginning of, and during the polymerization process,
samples were taken from the reactor and analysed in order to
follow the progress of the conversion of butadiene and macro-
monomer. The conversion of butadiene was determined gravime-
trically and the conversion of macromonomers by means of SEC
analysis.

Analytical determination of macromonomers and conversion of butadiene and macromonomer:

The butadiene conversion was determined gravimetrically
from the sample amount and from the weighed polymer amount. The
macromonomer conversion was determined by means of SEC analysis.
For this purpose approximately 10 mg of the polymer sample were
dissolved in 5 ml of THF and the solution was then analysed in
a HPLC apparatus made by KNAUER using a Shodex 80 M/S column.
The flow rate amounted to 1 ml/min and UV detection was carried
out at 254 nm. The evolution of the chromatograms with regard
to molecular mass and peak area respectively was accomplished
by an integrator Shimadzu C-R 3 A. The macromonomer conversion
was calculated from the UV peak areas for the detected poly-
styrene content in the high and low molecular range.

Results and discussion

In order to determine the macromonomer conversion by means
of SEC analysis it was first necessary to check whether the
molecular mass of the macromonomers had any influence on UV
activity. For this purpose and in order to study the influence
of the molecular mass of the macromonomers on their reactivity

Table 1:

Makrom./PS	$\bar{M}_n$ theor g/mol	$\bar{M}_n$ SEC g/mol	$\bar{M}_w/\bar{M}_n$	A_{UV} $10^6 \mu VS$	A_{MA}/A_{PS}
PS 2 S	2000	1640	1,20	13,9	5,35
PS 5 S	5000	4300	1,16	7,3	2,81
PS 9 S	9000	8300	1,20	5,67	2,19
PS 14 S	14000	14200	1,21	4,41	1,69
PS 30 S	30000	33500	1,20	3,86	1,29
PS 35 S	35000	38000	1,19	3,21	1,23
PS 2	2000	2100	1,04	2,58	
PS 9	9000	9000	1,07	2,65	
PS 50	50000	53000	1,09	2,53	

in copolymerization with butadiene /6/ the macromonomers and
polystyrenes listed in table 1 were synthesized, allowing for
a relatively wide variation in the molecular mass. The data for
the UV activity of the macromonomers and polystyrenes already
show that the former clearly exhibit differences. These data
are graphically represented in figure 1. From this diagram a
clear decrease in the UV activity of the macromonomers with
increasing molecular mass can be established. On the other hand
polystyrenes of differing molecular masses do not exhibit a
change in UV activity.

A representation of UV activity as a function of $1/\bar{M}_n$
shows an almost linear dependence of the values of the
macromonomers and a point of intersection on the ordinate with
the straight line representing the values of polystyrene. This
indicates that UV activity of macromonomers consists of two
portions; that of the polymer chain and that of the terminal
styryl function.

While the first amount is independent of the molecular mass,
the second increases with an increase in concentration of the
styryl head-group as this is proportional to $1/\bar{M}_n$.

Thus for the ratio between UV activity of stytyl-termi-
nated polystyrene macromonomers and polystyrene
$(A_{MA}/A_{PS} = F_{MA})$ the following mathematical correlation can be
established by means of least squares regression:

1. by applying the linear regression for any straight line of
   the form:

   $$F_{MA} = a \cdot 1/\bar{M}_n + b$$

the result is a regression line with a gradient
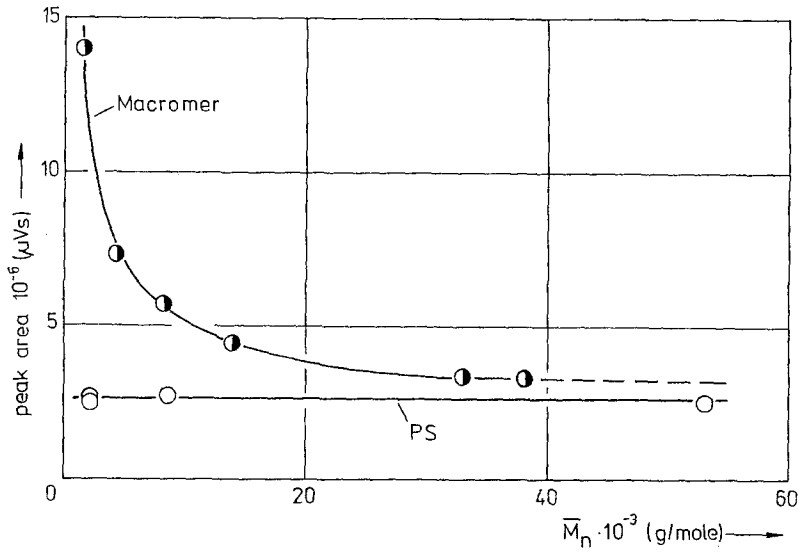a = 6922 ± 558 and b = 1,17 ± 0,152.

Figure 1: Peak area of polystyrene and macromonomers as a
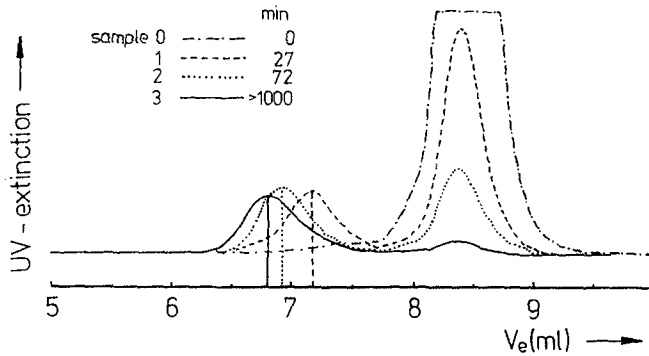function of molecular mass

Figure 2: Elution chromatograms of
samples at different con-
version

2. Taking the linear equation:

$$F_{MA} = 1 + a \cdot 1/\bar{M}_n \text{ as a basis}$$

the compensation computation will result in a straigth line
with a gradient of a = 7339 ± 354

Working on the assumption that the UV activity of the resul-
ting backbone polymer (in our case polybutadiene) is negligible
in comparison with polystyrene, the macromonomer conversion can
be ascertained from the peak areas of macromonomer (A_{MA}) and
graft polymer*). In doing so the higher UV activity of the un-
converted polystyrene macromonomer has to be considered by in-
cluding the value for F_{MA} as follows:

$$C_{MA} = \frac{A_{GP}}{A_{GP} + A_{MA}/F_{MA}} \quad \text{with } A_{GP} = \text{peak area of the graft polymer}$$

In the way illustrated above the anionic copolymerization of
butadiene and polystyrene macromonomers with an almost statisti-
cally ideal distribution of the grafts along the backbone chain,
could be carried out for the first time /6/.

On the analytical basis previously described the conversion-
time behaviour of macromonomers and butadiene during copolymeri-
zation could be ascertained.

Figure 2 shows the SEC diagrams of a few samples taken from
an experiment involving the copolymerization of butadiene and
macromonomer. From the graph it can be seen that the SEC peak
of the macromonomer decreases continuously and a UV-active high-
molecular product is formed with a molecular mass increasing in
time.

Figure 3 shows the ascertained conversion-time behaviour
using the macromonomer PS5S ($\bar{M}_n$ = 4 300 g/mole). By graphically
plotting the macromonomer conversion as a function of the buta-
diene conversion, the result is the course shown in figure 4.
From both figures it can be seen that by applying the initiator
system - n-butyl lithium/sodium tert-butanolate - and the macro-
monomer with $\bar{M}_n$ = 4 300 g/mole in this "living" copolymerization
process the insertion is regular and nearly complete because the
deviation of both curves in figure 3 or the deviation from the
ideal line, indicated by a dotted line, in figure 4 is only
small. This is in accordance with literary sources /8/ for this
type of initiator and the copolymerization of butadiene and
styrene. The macromonomers with higher molecular masses partially
exhibit even more distinct deviations from the ideal behaviour
in their reactivity /9/.

From the behaviour of the insertion of both comonomers con-
clusions can be drawn concerning the construction of the graft
copolymer. In this case it means that the polystyrene grafts
are statistically speaking nearly regularly distributed along
the polybutadiene backbone.

*)If the UV activity of the backbone polymer cannot be neglec-
ted the macromonomer conversion has to be ascertained by
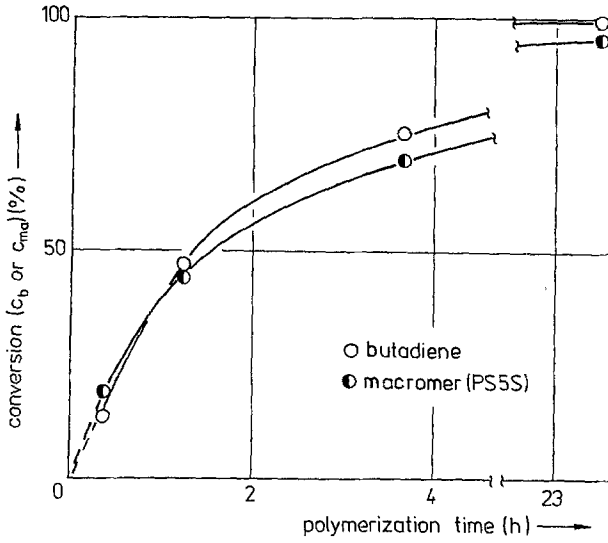means of double dedection /7/.

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Figure 3: Plots of the conversion of butadiene
and macromonomer ($\bar{M}_n$ = 4 300 g/mole)
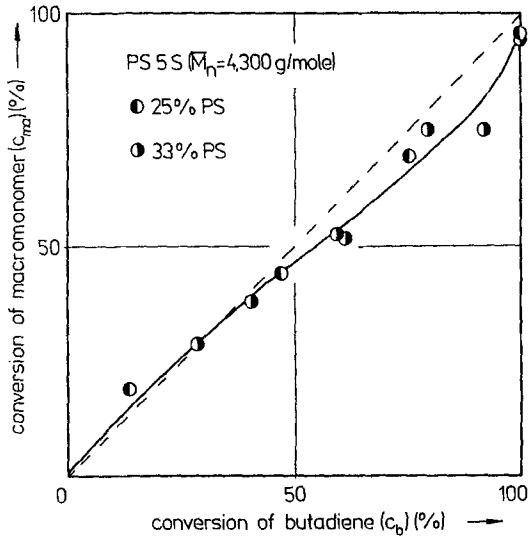versus polymerization time

Figure 4: Consumption of macromonomer
($\bar{M}_n$ = 4 300 g /mole) depen-
ding on the conversion of
butadiene

References

/1/ W. Hoffmann; Kunststoffe 77/8(1987) 767
/2/ D. S. Campbell; in "Developments in Block-Copolymers-2",
    ed. J. Goodman, Applied Science Publishers, New York,
    1985
/3/ J. P. Kennedy, C. Y. Lo; Polym. Bull. 13(1985) 441
/4/ R. Asami, M. Takaki, H. Hanahata: Macromolecules 16
    (1983)628
/5/ S. Kondo et al.; J. Macromol. Sci., Chem. A 13 (1979) 767
/6/ M. Arnold, W. Frank: 2nd Dresden Polymer Discussion,
    Part 1 (1989) 146
/7/ M. Niwa, T. Hayashi, M. Akahori; J. Macromol. Sci. A 24
    (1987) 49
/8/ C. F. Wofford, H. L. Hsieh; J. Polym. Sci., A- 1, 7
    (1969) 461
/9/ M. Arnold, W. Frank, G. Reinhold; Macromol. Chem. Rapid
    Commun. in preparation