Polymer Bulletin 2, 713–718 (1980)

Polymer Bulletin

Syntheses and Polymerizations of Macromers

I. Synthesis of p-Vinylbenzyloxyl Poly(Tetrahydrofuran) Macromer and Its Radical Polymerization

Ryuzo Asami, Mikio Takaki, Kazuo Kita and Eiji Asakura

Department of Synthetic Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

SUMMARY

Living poly(tetrahydrofuran) (PTHF) was coupled with sodium p-vinylbenzyloxide quantitatively to prepare a macromer of p-vinylbenzyloxyl poly(tetrahydrofuran) (VBO-PTHF). The radical polymerization of the macromer with AIBN was performed. From the GPC measurement the conversion of the macromer to poly-macromer was shown to be high percentage, but the degree of polymerization of poly-macromer was much lower than that expected in the case of regular monomers such as styrene.

INTRODUCTION

Recently, a polymer having a polymerizable group, which is called "macromer", has become of interest (NITADORI and TSURUTA, 1979). The homopolymerization of macromer having a polymerizable group at the chain end may give a well-defined comb-shaped polymer which has the highest graft density, and the oligomerization of the macromer may provide a star-type polymer. Also, the copolymerization with another monomer may give a novel graft copolymer which has not been obtained so far by the conventional graft copolymerization and grafting polymer reaction.

We have been much interested in macromer and have been planning a series of studies on the syntheses and polymerizations of macromers. First of all, the

0170-0839/80/0002/0713/$01.20

preparation and radical polymerization of VBO-PTHF were investigated; i.e., the macromer was prepared by the coupling reaction of living PTHF with sodium p-vinylbenzyloxide, which was polymerized with a radical initiator.

EXPERIMENTAL

Living PTHF was prepared by the polymerization of THF with triethyloxonium tetrafluoroborate which was synthesized according to MEERWEIN (1966) by using a vacuum line. Sodium p-vinylbenzyloxide was obtained by the reaction of NaH with p-vinylbenzyl alcohol in THF. 1-Methoxy-2-(p-vinylbenzyloxy)ethane ($CH_2=CH-$  $CH_2OCH_2CH_2OCH_3$) was prepared as described previously (ASAMI and NAKASHIMA, 1975).

The coupling reaction of living PTHF with sodium p-vinylbenzyloxide was carried out at 0°C by adding dropwise the THF solution of the former into that of the latter in a high vacuum system (ca. 10^{-5} mmHg). The reaction mixture was poured into a large amount of methanol -water (3:1, v/v) at 0°C. The precipitated polymer was purified by the reprecipitation and then dried *in vacuo*. The macromer was polymerized at 60°C by using α,α'-azobisisobutyronitrile (AIBN) as initiator. The conversion of the macromer to poly-macromer and the degree of polymerization of the poly-macromer were determined by GPC.

RESULTS AND DISCUSSION

As shown in Figure 1, the UV spectrum of a polymer obtained in the reaction of living PTHF with sodium p-vinylbenzyloxide was quite similar to that of 1-methoxy-2-(p-vinylbenzyloxy)ethane which is regarded as a model compound of VBO-PTHF macromer. The UV absorption of PTHF at 252 nm is negligible in comparison with that of p-vinylbenzyloxyl groups. Therefore, the amount of p-vinylbenzyloxyl groups was determined by using the molar extinction coefficient of the model compound ($\varepsilon_{max} = 1.59 \times 10^4$ at $\lambda_{max} = 252$ nm).

Table I shows the result of preparation of VBO-PTHF under various conditions. VBO-PTHF macromers thus obtained under these reaction conditions were characterized and the extent of coupling was estimated as given in Table II. The molecular weights of VBO-PTHF macromers were determined by four methods, i.e., intrinsic viscosity, vapor pressure osmometer (VPO), GPC, and end-group analysis. Consistent data were obtained by the four different methods. Especially, the agreement between the molecular weight by the VPO

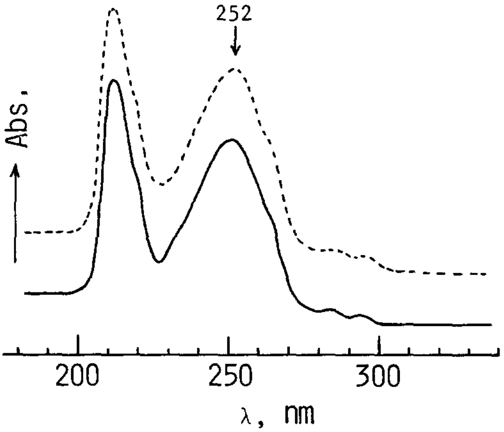

Figure 1. UV spectra of VBO-PTHF (——) and its model compound (1-methoxy,2-(p-vinylbenzyloxy)-ethane, - - -).

Table I

Preparation of VBO-PTHF

Expt no.	Living PTHF				Coupling reaction			Polymer yield,[b]	
	THF, ml	O^{+}[a], mmol	Temp, °C	Time min	[ONa]/[O^{+}]	Temp, °C	Time, min	gr	%
M03-1	87.3	0.636	0	20	1.35	0	120	0.87	1.12
M06-1	44.5	0.367	0	40	1.28	0	120	2.13	5.38
M10-1	33.8	0.270	r.t.	14	1.41	r.t.	34	2.32	7.75
-2	42.5	0.311	0	60	1.26	0	120	2.57	6.81
-3	81.4	0.578	0	60	1.26	0	120	4.82	6.67
M34-1	45.9	0.324	0	150	1.29	0	180	8.00	19.6

[a] Amount of the initiator (Et_3OBF_4). [b] Based on THF.

Table II

Characterization of VBO-PTHF and the Estimation of the Extent of Coupling

Expt no.	VBO-PTHF							II/O^{+}[d]	E.C.[e]
	[η], dl/g	Mol. wt.[a] $\times 10^{-3}$, Visc.	VPO	GPC	C=C	Amount (I),[b] mmol	C=C (II),[c] mmol		(II/I), %
M03-1	–	–	2.7	2.8	2.5	0.322	0.345	0.54	107
M06-1	0.205	6.6	5.6	5.7	5.7	0.380	0.374	1.02	98
M10-1	0.297	10.6	9.7	10.2	10.4	0.239	0.223	0.83	93
-2	0.285	10.0	9.1	9.0	8.9	0.282	0.288	0.93	102
-3	–	–	9.3	10.2	10.0	0.518	0.482	0.83	93
M34-1	0.722	33.6	–	36.0	32.0	0.238	0.250	0.77	105

[a] Molecular weights of VBO-PTHF based on intrinsic viscosity, vapor pressure osmometer, GPC, and end-group method. [b] Amount of VBO-PTHF in mmol, which was evaluated from the polymer yield (in Table I) and the molecular weight by VPO, except for Expt M34-1 based on the intrinsic viscosity method. [c] Amount of C=C groups in VBO-PTHF, which was spectroscopically determined. [d] O^{+} is noted in Table I. [e] Extent of the coupling, viz., II/I.

Table III

Radical Polymerization of VBO-PTHF[a]

Expt no.	VBO-PTHF Sample no.[b]	gr	Benz, gr	AIBN, wt%	Conv. of VBO-PTHF[c] GPC %	UV %	D.P.[d]
P10-1	M10-3	0.498	0.546	0.20	52	57	6.6
-2	"	0.510	0.529	0.28	48	56	6.3
-3	"	0.490	0.347	0.70	70	78	6.0
-4	"	1.17	1.02	1.09	60	76	4.3
P03-1	M03-1	0.299	0.306	0.50	74	80	9.9
-2	"	0.399	0.467	5.07	84	94	2.6

[a] Polymerization time, 20 hr; temp, 60°C. [b] For example, VBO-PTHF of M10-3 was VBO-PTHF obtained in Expt M10-3 in Table I. [c] Conversion of VBO-PTHF was determined by the GPC method and the UV method; i.e., the former based on the ratio of two peak areas and in the latter the amount of C=C remained was spectroscopically determined. [d] Estimated from GPC counts of the macromer and poly-macromer.

method and that calculated from the end-group analysis is taken to indicate that each VBO-PTHF molecule has a p-vinylbenzyloxyl group. The value of II/I shows the extent of coupling of living PTHF with sodium p-vinylbenzyloxide. Therefore, it is found that living PTHF is coupled with the sodium salt quantitatively regardless of the variation of the initiator efficiency which is shown by the value of II/O$^+$, even in the case of a low efficiency of 54% in Expt M03-1 in Table II.

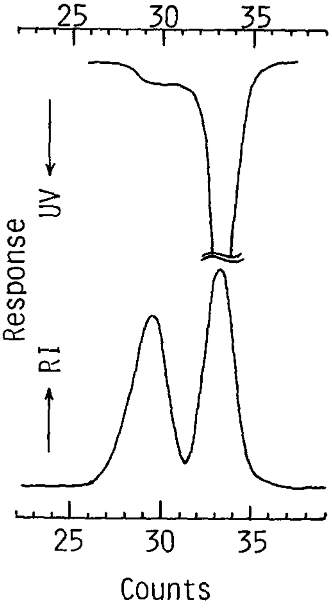

Figure 2. Typical GPC curves (RI and UV detectors) of the polymer obtained in Expt P10-1.

Table III shows the result of the radical polymerization of VBO-PTHF. As the amount of AIBN was increased, the conversion of the macromer to poly-macromer was increased whereas the degree of polymerization of poly-macromer was decreased. As the molecular weight of VBO-PTHF was increased from 3 x 10^3 (M03-1) to 1.0 x 10^4 (M10-3), the degree of polymerization of poly-macromer varied from 10 to 7, and the conversion of the macromer to poly-macromer decreased appreciably. It is the most interesting that in the radical polymerization of macromer the degree of polymerization of poly-macromer is much lower than that expected in the case of regular monomers such as styrene. As shown in Figure 2, the GPC curve of the polymer obtained in Expt P10-1 consists of two sharp peaks; apparently, one is ascribed to the macromer and the other is ascribed to its polymer.

From the facts mentioned above, it is suggested that in the radical polymerization of the macromer the rates of propagation and termination are much suppressed by the steric hindrance and by decreased mobility of macromer whereas the rates of chain transfers to the solvent and to the ether groups of PTHF chain would not be affected by the steric hindrance and diffusion control. For the detailed discussion on this novel kinetic feature in the radical polymerization of the macromer, further experiments including those of the ionic polymerization are in progress now.

REFERENCES

ASAMI, R. and NAKASHIMA, M., Polym. Prepr. (Jpn), 24 No. 1, 191 (1975)

MEERWEIN, H., Org. Syn., 46, 113 (1966)

NITADORI, Y. and TSURUTA, T., Kobunshi (high polymers), 28, 192 (1979)

Received May 6 / Accepted May 12, 198o