Hydrophilic–hydrophobic two-component polymer networks: 1. Synthesis of reactive poly(ethylene oxide) telechelics

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1,2,4-Triazoline-3,5-dione groups are attached to the ends of poly(ethylene oxides) of different chain lengths in a sequence of polymer analogous reactions. The 1,2,4-triazoline-3,5-dione group is a highly reactive functional group for Diels–Alder and 'ene' reactions at room temperature in quantitative yield. The functionality of the reactive telechelics is 1.9–2.0. The hydrophilic poly(ethylene oxide) chains with α,ω-1,2,4-triazoline-3,5-dione groups can be used to crosslink hydrophobic polymers like polybutadiene to obtain poly(ethylene oxide)-*linked*-polybutadiene two-component networks.

(Keywords: poly(ethylene oxide); telechelics; 1,2,4-triazoline-3,5-diones; two-component networks)

INTRODUCTION

Multicomponent polymer systems are of considerable interest as tailormade materials for specific applications. Control of phase morphology in phase-separated multicomponent systems may be achieved by a large variety of synthetic routes. In principle, the components are combined in a more or less well defined chain topology. The microphase morphology in phase-separated systems is then governed by the balance of the surface free energy (since immiscible polymers tend to form small internal surface areas) and contributions of the configurational entropy. Several comprehensive surveys are available, in which the basic principles of structure–property relationships are outlined[1–4]. Some of the most important chain topologies are:

(a) block copolymers;
(b) graft copolymers;
(c) interpenetrating networks (IPNs); and
(d) semi-interpenetrating networks (semi-IPNs).

Another type of crosslinked multicomponent chain topology may be obtained by using an end-functionalized polymer A as a crosslinker for polymer B (*Figure 1*). Such a topology is formally located between graft copolymers and interpenetrating networks. According to the systematic nomenclature of multicomponent polymer chain topologies, proposed by Sperling[5], this chain topology should be named 'coterminously linked copolymers'. If a polymer component A acts as crosslinker for polymer B, a preferable nomenclature would be poly(A)-*linked*-poly(B) two-component networks.

We have used this chain topology to obtain networks consisting of a hydrophilic and a hydrophobic polymer. The degree of phase separation, the size of the phase-separated domains and the hydrophilic–hydrophobic balance in such two-component networks can be changed by varying the component properties.

Low-molecular-weight poly(ethylene oxide) (PEO) was used as the hydrophilic polymer component. The terminal hydroxy groups in PEO make this polymer a convenient starting material for the preparation of a highly reactive telechelic system. The structure of the final poly(ethylene oxide)-*linked*-poly(B) can be altered by varying:

(a) the length of the PEO chains;
(b) the crosslink density; and
(c) the molecular characteristics (molecular weight, glass transition temperature, hydrophobicity) of the hydrophobic component.

The hydrophilic–hydrophobic balance will depend upon:

(a) the occurrence of phase separation;
(b) the elasticity of the hydrophobic component; and
(c) the morphology of the two-component network.

A network of the desired topology can be obtained by transforming the hydroxy end groups in polymerizable functions, i.e. by reaction with methacroyl chloride, and copolymerization of this telechelic polymer with a convenient monomer. A more defined network structure may be obtained if the molecular weight of polymer B is known, i.e. first each component, poly(A) and poly(B), is synthesized and network formation is performed in a separate reaction.

To achieve a defined quantitative crosslink reaction, the hydroxy end groups must be transformed into a functional group of high reactivity.

We choose 1,2,4-triazoline-3,5-dione as the functional group to react with polybutadiene. This functional group reacts rapidly and quantitatively with double bonds having allylic hydrogens, in an ene-type reaction[6–9]. In the present paper we report on the synthesis of highly reactive α,ω-di(4,4'-(1',2',4'-triazoline-3',5'-dione)-phenylene)-poly(ethylene oxides) (hereafter called XX-8; see later) as an intermediate in the preparation of poly(ethylene oxide)-*linked*-polybutadiene two-component networks[10].

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GENERAL REMARKS

Several problems arise in the synthesis of functionalized PEOs, as follows. Because of the good solubility of PEO and most of its derivatives in common organic solvents[11], difficulties may arise in the purification of reaction intermediates. Secondly, the high affinity of PEO towards water[11] may cause problems when moisture-sensitive derivatives are synthesized. Finally, chain scission may occur[12].

The synthesis of the desired reactive oligomers requires mild reaction conditions, and large conversions at a low level of side reactions.

In general, spectroscopic techniques in combination with molecular-weight measurements and elemental analysis were used to characterize the extent of reaction, the functionality and the purity of the materials.

The attachment of the 1,2,4-triazoline-3,5-dione heterocycle to the end of the polyether chain may be done either by direct coupling of a functionalized 1,2,4-triazolidine-3,5-dione and subsequent oxidation to the 1,2,4-triazoline-3,5-dione or by stepwise synthesis of the heterocycle at the end of the polyether chains in a series of polymer analogous reactions.

A possible starting compound for the first approach would be 4-(4′-methoxycarbonyl-phenylene)-1,2,4-triazolidine-3,5-dione[13]. The direct trans-esterification of this compound with PEO failed[14], probably due to the hydrolysis of the ester by the acidic 1,2,4-triazolidine-3,5-dione group. Similarly, an attempted direct etherification of 4-(4′-hydroxyphenylene)-1,2,4-triazolidine-3,5-dione[15,16] with PEO failed.

RESULTS AND DISCUSSION

In the following, a straightforward stepwise synthesis of the desired compound XX-8 (see later for meaning of this nomenclature) with different polyether chain lengths is given. Three commercial PEOs have been used, designated 200, 600 and 6000; all reactions were first tested using triethyleneglycol (TEG) as a model compound. In the second column of *Table 1* the molecular weights of the starting materials (XX-1), where XX is the designation for the different materials (i.e. 200, 600 and 6000), determined by vapour-pressure osmometry (v.p.o.) are listed.

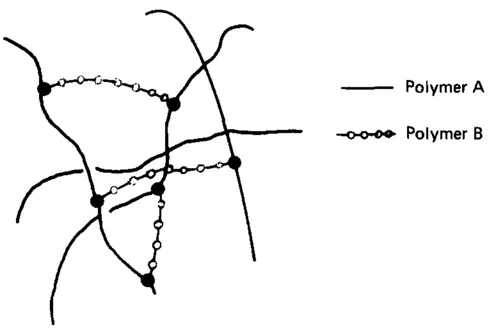

Figure 1 Schematic representation of a two-component polymer network obtained by crosslinking of polymer A with polymer B

The reaction scheme is given in *Figure 2*. In the first step, PEO XX was added in a nucleophilic aromatic substitution to 1-fluoro-4-nitrobenzene[17] to form the α,ω-di(4-nitrophenylene)-poly(ethylene oxides) (XX-2). This first reaction step requires the most drastic reaction conditions (195°C, several days). The degree of conversion can be monitored by the disappearance of the O–H stretching vibration in the infra-red spectrum (*Figure 3*). The time required for complete reaction increases with the polyether chain length. A similar dependence is observed for the subsequent reactions. For the derivatives 200-2 and 600-2 as well as for the triethyleneglycol derivative (TEG-2), no chain scission occurred. The good agreement between the degree of polymerization determined either by v.p.o. or ^{1}H n.m.r. end-group analysis shows that the substitution occurred quantitatively. For 6000-2, X_n was lowered, but the substitution is quantitative with respect to the reduced chain length.

By reduction of the nitrophenylenes (XX-2) using N_2H_4/Pd/C, the corresponding amines (XX-3) were obtained[17]. The extent of reduction can be determined by ^{1}H n.m.r. spectroscopy (*Figure 4*). The diamines 200-3 and 600-3 are viscous oils; traces of N_2H_4 are removed under vacuum. Under these conditions the low-molecular-weight chains in 200-3 evaporate partly and cause the observed increase in the number-average degree of polymerization (*Table 1*).

To avoid the high reaction temperatures required in the direct phosgenation of the diamines[18,19], the diamines were reacted with chlorotrimethylsilane to form the α,ω-di(4-(N-trimethylsilyl)-aminophenylene)-poly(ethylene oxides) (XX-4)[20]. After careful drying, these were reacted with phosgene to give the α,ω-di(4-N-isocyanatophenylene)-poly(ethylene oxides) (XX-5)[21]. The isocyanates were directly converted to the α,ω-di(4-semicarbazoyl(4′-ethoxycarbonyl)-phenylene)-poly(ethylene oxides) (XX-6). The formation of semicarbazides by reaction of isocyanates with ethylcarbazate is reported in the literature[22]. The derivative 6000-6 can be purified by recrystallization from ethanol: by filtration of the hot ethanol solution the insoluble lower-molecular-weight derivatives are separated. This explains the increase of the degree of polymerization observed for 6000-6 (see *Table 1*). The lower-molecular-weight derivatives 200-6 and 600-6 were purified by extensive washing with a non-solvent. By comparison of the ethylic

Table 1 Molecular-weight characterization for the various derivatives (XX-*i*) of the different molecular weight poly(ethylene oxides) (XX)

	XX-1 –OH		XX-2 $-\phi$–NO_2		XX-3 $-\phi$–NH_2	XX-4 $-\phi$–NH–$Si(CH_3)_3$	XX-6 –NHCONHNHCOEt	XX-7 $-\phi$–urazole
XX	M_n	P_n	M_n	P_n	P_n	P_n	P_n	P_n
200	217	4.5	455	4.4	6.0	6.2		6.1
600	630	13.9	834	13.1	13.0	14.1	12.8	13.0
6000	4200	95.0	3100	65	68.0		78.0	102.0

The molecular weights of samples 200-*i* and 600-*i* were obtained from ^{1}H n.m.r. and v.p.o. (when soluble in $CHCl_3$, XX-1 and XX-2); the data for series 6000-*i* were obtained from v.p.o.

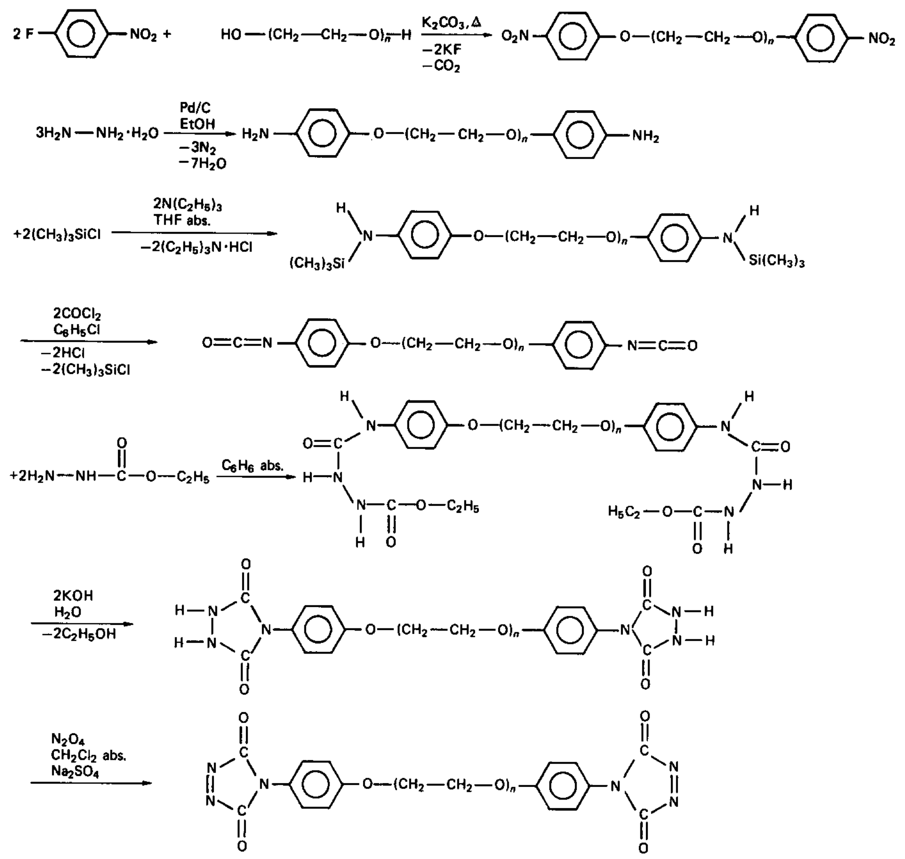

Figure 2 Reaction scheme for the synthesis of reactive telechelic PEO derivatives

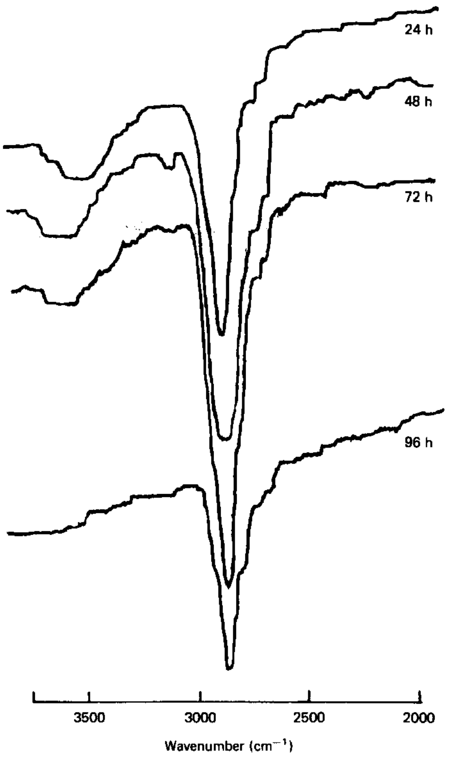

Figure 3 Decrease of the O–H stretching vibration (3500 cm^{-1}) during the reaction of PEO with 4-fluoronitrobenzene

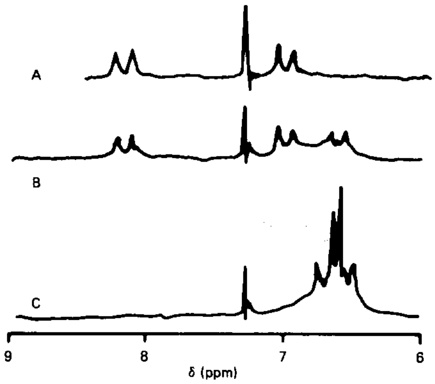

Figure 4 ^{1}H n.m.r. spectra in the region 6–9 ppm for different extents of reaction during the reduction of the nitro compound (XX-2): A, start of the reaction; B, about 50% conversion; C, end of the reduction

and aromatic hydrogens, the functionality is 2 for 200-6 and 600-6 and about 1.9 for 6000-6.

Ring closure of XX-6 to the α,ω-di(4,4′-(1′,2′,4′-triazolidine-3′,5′-dione)-phenylene)-poly(ethylene oxides) (XX-7) was performed in aqueous potassium hydroxide solution. This method of ring formation works for aromatic derivatives[13]. While 6000-7 was purified by recrystallization from ethanol, 200-7 and 600-7 were purified by column chromatography. Before preparing the reactive crosslinkers α,ω-di(4,4′-(1′,2′,4′-triazoline-3′,5′-dione)-phenylene)-poly(ethylene oxides) (XX-8) by oxidation of XX-7 with N_2O_4[23], traces of impurities and water must be removed because 1,2,4-triazoline-3,5-diones are moisture-sensitive. Nevertheless, the small amounts of water that are formed during the final reaction step are absorbed by the highly hydrophilic polyether chains and can be detected in the i.r. spectra of XX-8.

The reactive telechelics XX-8 were reacted with polybutadienes to obtain the desired two-component networks. First results on the synthesis and the properties of these materials are given in a subsequent paper[10].

EXPERIMENTAL

Starting materials

Laboratory-grade triethyleneglycol (TEG) was dried under vacuum for 4 h. PEO 200 (200-1) and PEO 600 (600-1) were kept over molecular sieves (4 Å) for several days and then heated to 70°C under vacuum for 2 days. PEO 6000 (6000-1) was recrystallized three times from dry ethanol at 60°C. A small amount of $NaBH_4$ is added to the boiling solution to remove the final traces of water.

Synthesis of α,ω-di(4-nitrophenylene)-poly(ethylene oxides) (XX-2)

4-Nitrofluorobenzene, K_2CO_3 and hydroxy-terminated poly(ethylene oxide) are heated in a glass flask to 195°C under a nitrogen atmosphere. Heating was continued until the O–H stretching vibration had disappeared. The detailed reaction conditions and product characterization are given in *Table 2*.

Synthesis of α,ω-di(4-aminophenylene)-poly(ethylene oxides) (XX-3)

The nitro compound XX-2 and the catalyst (Pd/C 5%) are dispersed in ethanol. Hydrazine hydrate is slowly added at room temperature. The reaction mixture is heated to reflux for 16 h. Additional catalyst and hydrazine hydrate is added if the reduction is incomplete. The hot reaction mixture is filtered. For detailed reaction conditions and product characterization, see *Table 3*.

Synthesis of α,ω-di(4-(N-trimethylsilyl)-aminophenylene)-poly(ethylene oxides) (XX-4)

The amino compound (XX-3) and triethylamine were dissolved in dried tetrahydrofuran and boiled to reflux under a nitrogen atmosphere. Trimethylchlorosilane was added slowly under vigorous stirring. The reaction mixture was refluxed for another 30 min. The precipitated triethylamine hydrochloride was filtered after cooling to 0°C. The solvent is removed in a Rotavapor. For detailed reaction conditions and product characterization, see *Table 4*.

Synthesis of α,ω-di(4-N-isocyanatophenylene)-poly (ethylene oxides) (XX-5)

Phosgenation was performed according to standard laboratory descriptions in a glass flask equipped with a stirrer, condenser, dropping funnel, gas inlet and outlet. The reaction is performed in dry chlorobenzene. After cooling to 0°C, the appropriate amount of phosgene was dissolved in the chlorobenzene. A solution of XX-4 in chlorobenzene was added slowly under ice cooling. The reaction mixture was kept at low temperature for another hour before heating to 80°C for 3 h under a phosgene atmosphere. To complete the reaction and remove the excess phosgene, the mixture is kept at high temperature (120°C) for another 3 h. After cooling to room temperature, the reaction vessel is purged with argon. The solvent is removed at room temperature under vacuum.

Table 2 Synthesis of α,ω-di(4-nitrophenylene)-poly(ethylene oxides) (XX-2)

Compound		TEG-2	200-2	600-2	6000-2
Composition of the reaction mixture					
XX-1		15.0 g (0.1 mol)	12.0 g (0.06 mol)	15.0 g (0.025 mol)	40.0 g (0.009 mol)
p-Nitrofluorobenzene		42.3 g (0.3 mol)	30.0 g (0.21 mol)	10.5 g (0.075 mol)	7.6 g (0.055 mol) + 3.5 g (0.024 mol)[a]
K_2CO_3		14.0 g (0.1 mol)	9.0 g (0.065 mol)	3.45 g (0.025 mol)	3.0 g (0.022 mol) + 2.5 g (0.018 mol)[a]
Reaction time		36 h	60 h	72h	96 h
Temperature		195°C	195°C	195°C	195°C
Purification		Column chromatogr. (1) CH_2Cl_2 (2) CH_2Cl_2/MeOH	Column chromatogr. (1) CH_2Cl_2 (2) CH_2Cl_2/MeOH	Column chromatogr. (1) CH_2Cl_2 (2) CH_2Cl_2/MeOH	Recryst. in ethanol, extensive washing with ether
Remarks		Yellow cryst.	Yellow oil	Yellow oil	Yellow powder
Yield		31.3 g (79%)	18.9 g (69%)	18.2 g (86%)	15.1 g (35%)
Characterization					
T.l.c.		CH_2Cl_2:$R_f = 0.21$	MeOH:$R_f = 0.75$	MeOH:$R_f = 0.74$	
melting point		98°C			43°C
mol. wt (v.p.o.)		392	455±23	834±41	3100±300
P_n		3	4.4	13.1	65
Formula		$C_{18}H_{20}N_2O_8$	$C_{20.8}H_{25.7}N_2O_{9.4}$	$C_{38.4}H_{60.1}N_2O_{18}$	$C_{141}H_{407}N_2O_{69.5}$
Elem. anal. exp. (calc.) (%)	C	54.96 (55.12)	54.23 (54.85)	54.86 (54.77)	54.49 (54.61)
	H	4.90 (5.13)	5.54 (5.64)	7.46 (7.26)	8.73 (8.65)
	N	7.51 (7.15)	5.65 (6.15)	3.22 (3.35)	
I.r. spectr. ν (cm^{-1})		3100w, 3080w, 2915m, 1587vs, 1500vs, 1335vs, 1265vs, 1110vs	3095m, 3075m, 2890s, 1587vs, 1510vs, 1340vs, 1260vs, 1110vs	3070w, 2950–2880s, 1585s, 1510s, 1340vs, 1263s, 1150–1080vs	2890vs, 1590w, 1515w, 1250w, 1118s
N.m.r. spectr. δ (ppm) ($CDCl_3$, TMS)		8.11m(4H), 6.96m(4H), 4.24m(4H), 3.72m(8H)	8.15m(4H), 6.93m(4H), 4.22m(4H), 3.69m(17.8H)	8.22m(4H), 7m(4H), 4.22m(4H), 3.72m(50.2H)	8.12m, 6.98m, 3.61m

* Additional addition after 48 h reaction time

Table 3 Synthesis of α,ω-di(4-aminophenylene)-poly(ethylene oxides) (XX-3)

Compound	TEG-3	200-3	600-3	6000-3
Composition of the reaction mixture				
XX-2	30.4 g (0.09 mol)	17.6 g (0.039 mol)	14.1 g (0.017 mol)	14 g (0.005 mol)
$N_2H_4{\cdot}H_2O$	2 × 7.0 g (0.28 mol)	2 × 10.0 g (0.4 mol)	2 × 7.5 g (0.3 mol)	2 × 6.2 g (0.248 mol)
Pd/C	2 × 70.0 mg	2 × 50.0 mg	2 × 50.0 mg	2 × 70.0 mg
ethanol	70.0 ml	60.0 ml	100.0 ml	100.0 ml
Reaction time	2 × 16 h	2 × 16 h	2 × 16 h	2 × 16 h
Temperature	78°C	78°C	78°C	78°C
Purification	Recryst. in ethanol	Vacuum drying	Vacuum drying	Recryst. in ethanol
Remarks	White crystals	Dark oil (traces of Pd/C)	Dark oil (traces of Pd/C)	Grey powder
Yield	13.1 g (53.5%)	11.2 g (75%)	10.6 g (70%)	8.1 g (58%)
Characterization				
melting point	89°C			58°C
mol. wt (n.m.r.)	332	450 ± 23	770 ± 38	3180 ± 320[a]
P_n	3	6	13	68
Elem. anal.				
exp. (calc.) (%) C	65.01 (65.06)			54.77 (55.6)
H	7.10 (7.27)			9.05 (8.89)
N	8.44 (8.43)	5.92 (6.02)		
I.r. spectr. ν (cm^{-1})	3405s, 3320s, 2880s, 1620s, 1512vs, 1238vs, 1110vs	3440–3300s, 2880s, 1622m, 1512vs, 1238vs, 1150vs	3410w, 3340m, 2880vs, 1620m, 1510vs, 1239vs, 1150–1085vs	2890vs, 1627w, 1510w, 1239m, 1115vs
N.m.r. spectr. δ (ppm) ($CDCl_3$, TMS)	6.64m(8H), 4m(4H), 3.72m(8H), 3.35m(4H)	6.65m(8H), 4m(4H), 3.65m(20.1H), 3.4m(4H)	6.64m(8H), 4m(4H), 3.71m(48H), 3.46s(4H)	6.58m, 3.65m[b]

[a] V.p.o.

[b] No quantitative evaluation of the ratio of aromatic and methylene hydrogen atoms was made

Table 4 Synthesis of α,ω-di(4-(*N*-trimethylsilyl)-aminophenylene)-poly(ethylene oxides) (XX-4)

Compound	TEG-4	200-4	600-4	6000-4
Composition of the reaction mixture				
XX-3	15.0 g (0.045 mol)	10.5 g (0.027 mol)	15.3 g (0.02 mol)	13.5 g (0.004 mol)
triethylamine	10.6 g (0.105 mol)	10.1 g (0.1 mol)	5.05 g (0.05 mol)	1.11 g (0.004 mol)
trimethylsilyl chloride	11.3 g (0.105 mol)	10.7 g (0.1 mol)	5.35 g (0.05 mol)	1.19 g (0.011 mol)
THF (solvent)	120 ml	125 ml	100 ml	150 ml
Reaction time	1 h	2 h	2 h	2 h
Temperature	68°C	68°C	68°C	68°C
Purification	Vacuum drying	Vacuum drying	Vacuum drying	Vacuum drying
Remarks	Yellow cryst.	Red oil	Red oil	Brown powder
Yield	20.5 g (94%)	13.9 g (97%)	17.2 g (95%)	13.4 g (96%)
Characterization				
mol. wt (n.m.r.)	476	617	965	
P_n	3	6.2	14.1	
Elem. anal.				
exp. (calc.) (%) C	60.36 (60.46)			54.36 (55.49)
H	8.46 (8.44)			8.68 (8.95)
N	5.88 (6.01)			
I.r. spectr. ν (cm^{-1})	3450–3350s, 2870s, 1621m, 1511vs, 1240vs, 1066s, 843s, 756m	3440–3320s, 2890vs, 1625s, 1510vs, 1243vs, 1150–1050vs, 837s, 755m	3420w, 3340m, 2880vs, 1620m, 1510vs, 1240vs, 1150–1080vs, 845vs, 755m	
N.m.r. spectr. δ (ppm) ($CDCl_3$)	6.52m(8H), 4.04m(4H), 3.75m(8H), 3.17s(2H), 0.23m(18H)	6.62m(8H), 3.95m(4H), 3.57m(20.8H), 3.3s(2H), 0.05m(18H)	6.61m(8H), 4m(4H), 3.62m(54.6H), 0.1m(18H)	6.6m, 4m, 3.57m, 3.16s, 0.08m[a]

[a] No quantitative evaluation of the ratio of aromatic and methylene hydrogen atoms was made

The products were used for the subsequent reaction without further purification. The completion of the reaction was checked by the disappearance of the characteristic Si–C and Si–N vibrations and the appearance of the –NCO stretching vibration at $\tilde{\nu} = 2260\ cm^{-1}$. For detailed reaction conditions and product characterization, see *Table 5*.

Synthesis of α,ω-di(4-semicarbazoyl(4′-ethoxycarbonyl)-phenylene)-poly(ethylene oxides) (XX-6)

Ethylcarbazate is dissolved in dry benzene under a nitrogen atmosphere. Under vigorous stirring a solution of the isocyanate (XX-5) is added slowly. To complete the reaction, the mixture was first stirred at room temperature for 2 h before heating to reflux for another

Table 5 Synthesis of α,ω-di(4-*N*-isocyanatophenylene)-poly(ethylene oxides) (XX-5)

Compound	TEG-5	200-5	600-5	6000-5
Composition of the reaction mixture				
XX-4	16.3 g (0.04 mol)	13.8 g (0.027 mol)	17.2 g (0.017 mol)	13.4 g (0.004 mol)
phosgene	8.2 g (0.039 mol)	7.1 g (0.078 mol)	5.0 g (0.05 mol)	1.1 g (0.011 mol)
chlorobenzene (solvent)	200 ml	180 ml	120 ml	160 ml
Reaction time	8 h	8 h	8 h	8 h
Temperature	3 h: 80°C 3 h: 120°C	3 h: 80°C 3 h: 120°C	3 h: 80°C 3 h: 120°C	3 h: 80°C 3 h: 120°C
Purification	Vacuum drying	Vacuum drying	Vacuum drying	Vacuum drying
Remarks	Dark oil	Dark oil	Dark oil	Dark oil
I.r. spectr. ν (cm^{-1})	2260vs	2280vs	2260vs	2260vs

Table 6 Synthesis of α,ω-di(4-semicarbazoyl(4′-ethoxycarbonyl)-phenylene)-poly(ethylene oxides) (XX-6)

	TEG-6	200-6	600-6	6000-6
Composition of the reaction mixture				
XX-5	13.9 g (0.034 mol)	11.8 g (0.026 mol)	15.5 g (0.017 mol)	13.4 g (0.004 mol)
ethylcarbazate	7.8 g (0.075 mol)	7.0 g (0.067 mol)	5.2 g (0.05 mol)	1.0 g (0.009 mol)
benzene (solvent)	200 ml	140 ml	200 ml	140 ml
Reaction time	4 h	4 h	4 h	12 h
Temperature	2 h: room temp. 2 h: 65°C	2 h: room temp. 2 h: 65°C	2 h: room temp. 2 h: 65°C	2 h: room temp. 4 h: 65°C
Purification	Recryst. in CH_2Cl_2	Extensive washing with benzene	Extensive washing with benzene	Recryst. in ethanol
Remarks	White cryst.	Brown powder	Brown powder	Brown powder
Yield	13.6 g (68%)	12.3 g (75%)	14.1 g (70.5%)	10.5 g (67%)
Characterization				
melting point	158°C	112°C		43°C
mol. wt (n.m.r.)	592		1020	3900±400[a]
P_n	3		12.8	78±8
Elem. anal.				
exp. (calc.) (%) C	48.38 (52.70)		51.71 (53.47)	53.9 (54.2)
H	6.15 (6.12)		7.16 (7.40)	8.6 (8.7)
N	13.06 (14.18)		9.76 (8.20)	2.5 (2.2)
I.r. spectr. ν (cm^{-1})	3350–3180vs, 2920m, 1705vs, 1665s, 1375w, 1360w, 1270–1200vs, 1140–1085s	3350–3200s, 3030w, 1740–1690vs, 1600s, 1560–1540m, 1505vs, 1345w, 1250–1200vs, 1105s	3350–3220s, 2920m, 1720–1680vs, 1600m, 1510vs, 1250–1210vs, 1130–1080s	3350–3250w, 2880vs, 1720m, 1545w, 1510m, 1260s, 1060s
N.m.r. spectr. δ (ppm) (d_6-DMSO, TMS)	8.83s(2H), 8.46s(2H), 7.84s(2H), 7.30m(4H), 6.80m(4H), 4.0m(8H), 3.58m(8H), 1.2t(6H)		8.84s(2H), 8.61s(2H), 7.98s(2H), 7.45m(4H), 6.93m(4H), 4.22q(8H), 3.69m(47.3H), 1.3t(6H)	8.72s(2H), 8.4s(2H), 7.8s(2H), 7.4m(4H), 6.8m(4H), 3.95m, 3.53m, 1.14t(6H)

[a] V.p.o.

2 h. For detailed reaction conditions, purification and characterization, see *Table 6*.

Synthesis of α,ω-di(4,4′-(1′,2′,4′-triazolidine-3′,5′-dione)-phenylene)-poly(ethylene oxides) (XX-7)

The semicarbazide (XX-6) is dispersed in aqueous KOH (~4 m), stirred at room temperature for 2 h and then heated to reflux (2 h). The non-soluble fraction is separated by filtration. After cooling to 0°C, aqueous hydrochloric acid (~5 m) is added until the pH reaches 1. The precipitate is filtered and washed with water. For detailed reaction conditions, purification and characterization, see *Table 7*.

Synthesis of α,ω-di(4,4′-(1′,2′,4′-triazoline-3′,5′-dione)-phenylene)-poly(ethylene oxides) (XX-8)

The dried product (XX-7) and freshly dried Na_2SO_4 are dispersed in dry CH_2Cl_2. After purging with nitrogen (30 min) the reaction mixture is cooled to 0°C and dried and gaseous NO_2 is introduced into the reaction mixture, until the deep red colour formed remains. Excess NO_2 is purged out with nitrogen. Unreacted XX-7 and Na_2SO_4 are separated and the solvent is removed under vacuum. The remaining active crosslinkers are used for crosslinking with polybutadienes without further purification.

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Table 7 Synthesis of α,ω-di(4,4′-(1′,2′,4′-triazolidine-3′,5′-dione)-phenylene)-poly(ethylene oxides) (XX-7)

Compound	TEG-7	200-7	600-7	6000-7
Composition of the reaction mixture				
XX-6	12.5 g (0.021 mol)	11 g (0.016 mol)	13.5 g (0.013 mol)	9.5 g (0.0024 mol)
KOH	7.2 g (0.128 mol)	9 g (0.16 mol)	5.6 g (0.1 mol)	1.6 g (0.028 mol)
H_2O	70 ml	80 ml	100 ml	100 ml
Reaction time	5 h	5 h	5 h	5 h
Temperature	2 h: room temp. 3 h: 100°C	2 h: room temp. 3 h: 100°C	2 h: room temp. 3 h: 100°C	2 h: room temp. 3 h: 100°C
Purification	Raw product refluxed with THF, filtered, then solvent evaporated	Column chromatography	Column chromatography	Recryst. in ethanol
Remarks	White solid	Light brown powder	Light brown powder, contains traces of KCl	Grey solid
Yield	9.1 g raw product (85%)	4.2 g (40%)	7.6 g raw product	3.9 g (33%)
Characterization				
melting point		146°C (decomp.)		48°C
mol. wt (n.m.r.)	500	636	940	4880
P_n	3	6.1	13	102
Elem. anal.				
exp. (calc.) (%) C				54.3 (54.41)
H				7.7 (8.72)
N				1.5 (1.71)
I.r. spectr. ν (cm^{-1})	3300–3150m, 3090m, 2940m, 1760w, 1710–1690vs, 1252s, 1140–1090s	3450–3250s, 2910w, 1750w, 1720–1680vs, 1610vs, 1510vs, 1248vs, 1150–1060vs	3450–3300s, 3080w, 2920s, 1765m, 1710–1690vs, 1600w, 1510s, 1250s, 1150–1050vs	2880vs, 1760w, 1695m, 1510m, 1239m, 1110vs
N.m.r. spectr. δ (ppm) (d_6-DMSO, TMS)	8.1s(4H), 7.32m(4H), 7.01m(4H), 4.07m(4H), 3.6m(8H)	7.35m(4H), 6.96m(4H), 5s(4H), 4.07m(4H), 3.56m(20.5H)	7.31m(4H), 7m(4H), 6.55s, broad(4H), 4.1m(4H), 3.48m(48H)	7.3m, 4.35s, 3.5m

Table 8 Synthesis of α,ω-di(4,4′-(1′,2′,4′-triazoline-3′,5′-dione)-phenylene)-poly(ethylene oxides) (XX-8)

Compound	200-8	600-8	6000-8
Composition of the reaction mixture			
XX-7	0.7 g (1 mmol)	0.7 g (0.74 mmol)	2 g (0.4 mmol)
Na_2SO_4	40 g	40 g	80 g
CH_2Cl_2	200 ml	200 ml	200 ml
Reaction time	1.5 h	1.5 h	1.5 h
Purification	Vacuum drying	Vacuum drying	Vacuum drying
Remarks	Dark red powder	Red powder	Brown-red powder
Yield	0.45 g (65%)	0.36 g (52%)	1.7 g (85%)
I.r. spectr. ν (cm^{-1})	3450w, 2890m, 1760w, 1720–1700vs, 1600w, 1510vs, 1460m, 1255–1230s, 1150–1050s, 840s	3500w, 3080w, 2880vs, 1760m, 1730–1710vs, 1595m, 1510s, 1260–1240s, 1150–1060vs, 845s, 748m	3500w, 3080w, 2880vs, 1760–1730m, 1510w, 1460s, 1235s, 1105vs, 8315s

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