# Highly Selective Biphasic Telomerization of Butadiene with Glycols: Scope and Limitations

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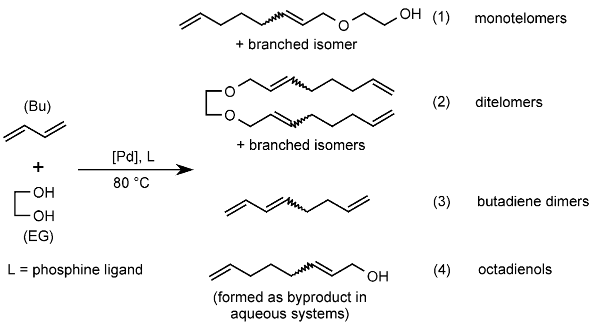
**Abstract:** Highly selective telomerization reactions of a number of short-chain glycol nucleophiles with 1,3-butadiene have been achieved in aqueous biphasic systems employing the water-soluble catalyst system Pd(acac)$_2$/TPPTS. For all substrates the selectivity for the obtained monotelomers **5–7** reached $\geq 95\%$ whereas butadiene dimers **3**, octadienols **4** and ditelomers like **2** were produced only in trace amounts. The order of reactivity is ethylene glycol >> 1,3-propylene glycol ≈ glycerol > 1,4-butylene glycol, which is in agreement with generally observed trends. The scope and limitations of these reactions are discussed in terms of obtained yields and achievable catalyst productivities (total turnover numbers).

**Keywords:** alcohols; biphasic catalysis; butadiene; C-C coupling; homogeneous catalysis; palladium; telomerization

## Introduction

The palladium-catalyzed telomerization of 1,3-dienes, originally discovered by Smutny in 1967,[1] still receives a great deal of attention in both academia and industry since the reaction offers great synthetic potential combined with broad scope.[2] Beller et al. reported significant improvements in the industrially interesting telomerization of butadiene (Bu) with methanol.[3–5] The industrial interest in this reaction is emphasized by patents[6,7] published recently. While monofunctional alcohols and other simple nucleophiles have been intensively studied over the past decade, di- und polyfunctional substrates like ammonia[8] have not been examined in such detail. In the past years, sucrose has been successfully telomerized to complex mixtures of sucrose ethers[9,10] suitable for specific applications. However, the production of 2,7-octadien-1-ol by hydrodimerization of butadiene is the only example of an industrial telomerization process so far in operation.[11] This is in part the consequence of problems often encountered in selectivity control and optimization of catalyst performance as well as catalyst recycling.

Telomerization reactions with glycols such as ethylene glycol (EG) demand effective methods of selectivity control if specific products are to be synthesized because the monotelomers primarily produced still possess reactive functionalities for consecutive reactions. The reaction of butadiene with ethylene glycol yields complex mixtures of monotelomers **1**, ditelomers **2** and butadiene dimers **3** when performed in single liquid phase systems[12] as shown in Scheme 1. The telomers usually contain about 5–10% branched isomers.



**Scheme 1.** Telomerization of butadiene with ethylene glycol.

From an industrial point of view, however, only the monotelomers **1** are of considerable interest as their saturated analogues can be used as plasticizer alcohols for polymers like PVC.[13] Other patents also focus on applications in the field of cosmetics and surfactants.[14–16] On the other hand, the ditelomers **2** and butadiene dimers **3** are of lower interest. As a consequence, efficient selectivity control is one major issue in these reactions. Also, the problem of effective catalyst recycling remains, which has to be solved in order to establish an industrially feasible process. Both issues cannot be managed easily in homogeneous liquid single phase systems.

Biphasic catalysis provides the potential to resolve both problems outlined above at the same time. The reader is referred to a review by Behr[17] and a very recent one by Keim.[18] Lately, we[19] have demonstrated a highly selective telomerization reaction of butadiene with ethylene glycol in aqueous biphasic systems

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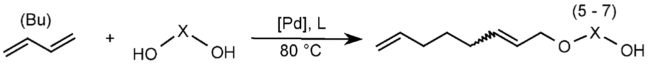
employing Pd(acac)$_2$/TPPTS as a water-soluble *in-situ* catalyst. The observed increase in selectivity is attributed to combined ligand and *in-situ* extraction effects. The desired monotelomers **1** were obtained in yields up to 80% and selectivities exceeding 95% while effective catalyst recycling was achieved using the liquid-liquid two-phase technique. Dimers **3**, ditelomers **2** and octadienols **4** were obtained as byproducts only in yields of 1–2% each. Octadienols **4** are formed in aqueous biphasic telomerization reactions of butadiene as a consequence of nucleophilic activity of the water solvent. We have also described the application of a telomerization-hydrogenation sequence as part of our green chemistry efforts.[20]

In this paper, we report the successful expansion of this reaction to a series of glycol substrates, namely 1,3-propylene glycol (PG), 1,4-butylene glycol (BG) and glycerol (Gly) as the products efficiently and selectively obtained are a useful addition to the group of monotelomer compounds. The reactivity of the different substrates is also compared in terms of yields and overall catalyst productivities. Finally, the scope and limitations of this reaction are discussed.

## Results and Discussion

### Aqueous Biphasic Telomerization of Butadiene with Short-Chain Glycol Substrates

In order to extend the recently reported aqueous biphasic telomerization methodology,[19] the substrates 1,3-propylene glycol (PG), 1,4-butylene glycol (BG) and glycerol (Gly) have been telomerized with 1,3-butadiene to yield the monotelomer products **5** to **7** as shown in Scheme 2.



L = TPPTS - ligand
X = (CH$_2$)$_3$ : substrate: PG; product: monotelomer (5)
X = (CH$_2$)$_4$ : substrate: BG; product: monotelomer (6)
X = CH$_2$-CH(OH)-CH$_2$ : substrate: glycerol; product: monotelomer (7)
byproducts : corresponding ditelomers, butadiene dimers (3) and octadienols (4)

**Scheme 2.** Biphasic telomerization of butadiene with glycol substrates.

All monotelomer products **5** to **7** were synthesized with very good selectivity (≥95%) whereas butadiene dimers **3**, octadienols **4** and the corresponding ditelomers were only produced as byproducts in yields of about 1–2% each. The aqueous-alcoholic catalyst phases obtained after the reactions were successfully recycled several times leading to high catalyst productivities. The results obtained for the different substrates are summarized in Tables 1 to 3.

With 1,3-propylene glycol (PG) and glycerol (Gly) maximum yields of telomers of roughly 60% were obtained (Nos. 3 and 12) while the maximum yields achievable with 1,4-butylene glycol (BG) were much lower (about 30%; No. 7). With PG and Gly, good yields of monotelomers could be achieved in four and three consecutive runs, respectively. With BG, however, already the first recycling run (No. 8) led to a poor result, which could not be improved in the following runs. As a consequence, total turnover numbers (TTNs) for monotelomer production of several thousands could be reached with the substrates PG and Gly, while the overall catalyst productivity remained below 1500 when BG was used as substrate. Obviously, the reactivity of the substrates depends on their molecular size or chain length. The decreasing catalyst activity observed is attributed to catalyst decomposition partly caused by oxidation of TPPTS to the corresponding phosphine

**Table 1.** Results of aqueous biphasic telomerization of butadiene with 1,3-propylene glycol.

| No. | Recycle | Products | | TON | TOF [h$^{-1}$][c] | TTN[d] |
|---|---|---|---|---|---|---|
| | | Yield **5** [%][a] | **3** [%][b] | | | |
| 1 | Start | 32 | 2 | 534 | 134 | 534 |
| 2 | 1 | 51 | 2 | 856 | 214 | 1390 |
| 3 | 2 | 56 | 2 | 946 | 237 | 2336 |
| 4 | 3 | 55 | 2 | 928 | 232 | 3264 |
| 5 | 4 | 18 | 1 | 296 | 74 | 3560 |
| 6 | 5 | 29 | 2 | 480 | 120 | 4040 |

**Conditions:** Bu/PG = 2.5/1; catalyst concentration: 0.06 mol % Pd(acac)$_2$ (based on PG) + TPPTS; P/Pd = 5/1; TPPTS supplementation: 2.5 equivs. per recycle; 10 mL H$_2$O; 25 mL PG; 80 °C; 4 h; stirrer velocity = 1200 rpm.

[a] Based on PG.

[b] Wt % of butadiene dimers in reaction mixture.

[c] Average over total reaction time.

[d] Total turnover number.

**Table 2.** Results of aqueous biphasic telomerization of butadiene with 1,4-butylene glycol.

| No. | Recycle | Products | | TON | TOF [$h^{-1}$][c] | TTN[d] |
|---|---|---|---|---|---|---|
| | | Yield **6** [%][a] | **3** [%][b] | | | |
| 7 | Start | 31 | 2 | 527 | 132 | 527 |
| 8 | 1 | 21 | 3 | 359 | 90 | 886 |
| 9 | 2 | 17 | 3 | 286 | 72 | 1172 |
| 10 | 3 | 17 | 2 | 292 | 73 | 1464 |

**Conditions:** Bu/BG = 2.5/1; catalyst concentration: 0.06 mol % $Pd(acac)_2$ (based on BG) + TPPTS; P/Pd = 5/1; TPPTS supplementation: 2.5 equivs. per recycle; 10 mL $H_2O$; 25 mL BG; 80 °C; 4 h; stirrer velocity = 1200 rpm.

[a] Based on BG.

[b] Wt % of butadiene dimers in reaction mixture.

[c] Average over total reaction time.

[d] Total turnover number.

**Table 3.** Results of aqueous biphasic telemerization of butadiene with glycerol.

| No. | Recycle | Products | | TON | TOF [$h^{-1}$][c] | TTN[d] |
|---|---|---|---|---|---|---|
| | | Yield **7** [%][a] | **3** [%][b] | | | |
| 11 | Start | 41 | < 1 | 694 | 174 | 694 |
| 12 | 1 | 58 | < 1 | 990 | 248 | 1684 |
| 13 | 2 | 52 | < 1 | 887 | 222 | 2571 |
| 14 | 3 | 20 | < 1 | 333 | 83 | 2904 |
| 15 | 4 | 23 | < 1 | 389 | 97 | 3293 |

**Conditions:** Bu/Gly = 2.5/1; catalyst concentration: 0.06 mol % $Pd(acac)_2$ (based on Gly) + TPPTS; P/Pd = 5/1; TPPTS supplementation: 2.5 equivs. per recycle; 10 mL $H_2O$; 25 mL Gly; 80 °C; 4 h; stirrer velocity = 1200 rpm.

[a] Based on Gly.

[b] Wt % of butadiene dimers in reaction mixture.

[c] Average over total reaction time.

[d] Total turnover number.

oxide. This effect has already been observed by another group[21] examining biphasic telomerization reactions with this catalyst system. One source of TPPTS oxidation is contamination with air during work-up of the biphasic reaction mixture, which cannot be totally avoided. To compensate for the loss of ligand by oxidation and decomposition, the separated aqueous catalyst phase was supplemented with an appropriate amount of fresh ligand solution prior to each recycle run. The leaching of palladium into the organic product phase associated with a residual water content of about 0.3 wt % has been previously examined[19] and is not considered to be the crucial cause of decreasing activity and yields. Unavoidable catalyst decomposition leading to palladium metal is responsible for these effects.

In order to compare the reactivity of all the glycol substrates examined, the overall catalyst productivities (TTNs) including those reported earlier for ethylene glycol[19] are given in Figure 1 as a function of the experiment number. The experimental series were continued until the obtained yields remained at a low level.

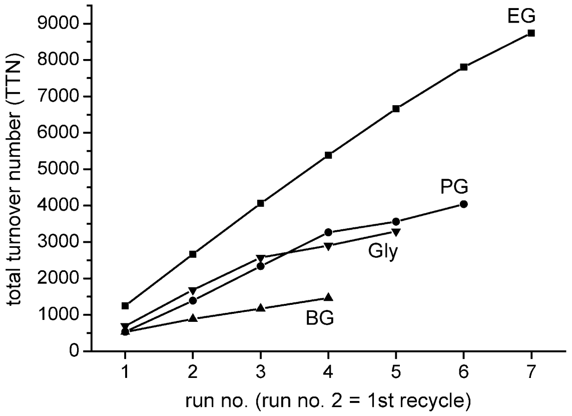


**Figure 1.** Overall catalyst productivities obtained during telomerization experiments with glycol substrates. **Conditions:** Bu/glycol = 2.5/1; cat. 0.06 mol % (based on glycol) $Pd(acac)_2$ + 5 equivs. TPPTS; ligand supplementation: 2.5 equivs. per recycle; 10 – 12 mL $H_2O$; 20 – 30 mL glycol; 80 °C; 1200 rpm; 4 h. Substrates: EG (■), PG (●), BG (▲), Gly (▼).

Ethylene glycol (EG) is by far the most reactive substrate. A total turnover number in the range of 9000 is possible after seven runs, which is more than twice as high as the value obtained with PG, the substrate possessing the second highest reactivity. PG and glycerol roughly show the same reactivity while BG is by far the least reactive substrate. Based on these data, the order of reactivity for the glycol substrates studied is: EG >> PG ≈ Gly > BG which is in agreement with the general trends reported in the literature. As a consequence, catalyst recycling using biphasic techniques is possible up to six times if EG is used as substrate. The catalyst phases can be successfully recycled four to five times with PG and Gly as substrates and with BG only a three-fold recycling is attractive. The best chances for an industrial application of this biphasic telomerization process are seen with ethylene glycol as substrate and therefore we are currently studying this reaction using the established miniplant technology.[22]

### Limitations of the Catalyst System Pd(acac)$_2$/TPPTS

In order to explore the limits of the catalyst system, many glycol substrates related to those described above have been tested. Special focus was laid on tolerance of increasing steric demands and different functional groups. Unfortunately the catalyst system Pd(acac)$_2$/TPPTS does not tolerate increasing steric demand at all. Both 1,2-propylene glycol [$CH_3$-CH(OH)−$CH_2$-OH] and 2,2-dimethyl-1,3-propylene glycol [HO−$CH_2$-C(Me)$_2$-$CH_2$-OH] were not telomerized to a significant degree under standard conditions. To test functional group tolerance, a range of different substrates was tested. The inability of the catalyst system to convert 2-*cis*-butene-1,4-diol [HO−$CH_2$-CH=CH−$CH_2$-OH] and 2-butyne-1,4-diol [HO−$CH_2$-C≡C−$CH_2$-OH] revealed its sensitivity against multiple bonds in the substrate, which apparently block the active species. Carboxylic acid functionalities are also not tolerated as both glycolic acid (HOOC−$CH_2$OH) and oxalic acid (HOOC−COOH) were not converted either as free acids or as sodium salts. The pH value of the solution does not seem to play a major role here. Finally, 1,3-dihydroxyacetone [HO−$CH_2$-C(O)−$CH_2$-OH] was tested without success both in presence and absence of 1 equiv. NaOH indicating intolerance against the carbonyl group.

These results show that the catalyst system Pd(acac)$_2$/TPPTS is only suitable for the selective telomerization of sterically undemanding short chain glycol substrates such as primary $C_2$ – $C_4$ glycols and glycerol as well as for the unselective telomerization of sugar substrates as found by others.[10] The best results in selective reactions can be obtained with the most reactive substrate ethylene glycol (EG).

## Conclusion

The aqueous biphasic telomerization methodology reported earlier[19] has been successfully transferred to sterically undemanding primary $C_3$ – $C_4$ glycols and glycerol. The corresponding monotelomers **5** to **7** have been synthesized with high selectivity ($\geq$95%) and in good yields (up to 60%). Byproduct formation was limited to butadiene dimers **3**, octadienols **4** and the corresponding ditelomers being produced in yields of 1 – 2% each. The catalyst system Pd(acac)$_2$/TPPTS could be recycled up to five times and for some substrates total turnover numbers of several thousands were achieved. The reactivity order of the substrates is consistent with general trends reported in the literature with ethylene glycol showing the highest activity. The catalyst system does not tolerate increased steric demands or functional groups like multiple bonds, carbonyl or carboxylic acid groups in the glycol substrates. Therefore, the application of the presented methodology is limited to the reported substrates. An industrially feasible telomerization process is envisioned using ethylene glycol (EG) as substrate, which is currently under investigation using miniplant technology.[22]

## Experimental Section

### Reagents, Catalysts and Handling

1,3-Butadiene (99.5%) and argon (99.998%) used as dried inert cover gas were purchased from Messer-Griessheim. Palladium(II) bis(acetylacetonate), Pd(acac)$_2$, was synthesized according to the literature.[23] Triphenylphosphinetrisulfonate (TPPTS) was obtained from Celanese AG as a 25 wt % aqueous solution of the trisodium salt. All other chemicals were purchased from common suppliers. All solvents were degasified and used saturated with argon. All reactions and handling were done under dry argon using standard Schlenk tube techniques.

### Aqueous Biphasic Telomerization of Butadiene with Glycol Substrates

63 mg (0.2 mmol) of Pd(acac)$_2$ and 2.3 g (1 mmol) of aqueous TPPTS solution were dissolved in 10 mL of deionized water and mixed with the appropriate amount of glycol substrate (25 – 30 mL; 0.35 mol), giving a clear bright yellow solution, which was transferred into an evacuated 300-mL stainless steel autoclave. 49 g (0.9 mol) of butadiene were condensed into the autoclave. The vessel was heated to 80 °C and stirred at 1200 rpm for 4 h. Consumption of butadiene could be followed by pressure drop from about 10 to about 5 bar. The vessel was cooled to ambient temperature and unreacted butadiene was burnt through a custom-made safety nozzle. The autoclave was opened and the biphasic content poured into a separating funnel. 100 mL of cyclohexane were added, the mixture was

shaken vigorously and the phases were allowed to separate over a period of 15 minutes. The lower phase consisting of the aqueous catalyst solution and unreacted substrate was separated and stored under argon. Cyclohexane was removed from the upper organic phase under reduced pressure (200 mbar, 50 °C) and recycled. The residue was analyzed by GC and Karl-Fischer titration. The catalyst solution obtained was supplemented with 1.15 g (0.5 mmol) aqueous TPPTS solution and mixed in a Schlenk-tube with the appropriate amount of glycol substrate, giving a clear yellow solution that was used once again for the telomerization reaction as described above.

### Analysis and Product Characterization

Routine gas chromatographic analyses were done on an HP 6890 instrument (Hewlett-Packard GmbH, Waldbronn, Germany) equipped with an FI detector and an HP-INNOWax capillary column (30 m, coating polyethylene glycol, diameter 0.25 mm, film thickness 0.25 μm) in connection with an autosampler. GC/MS data were recorded on a HP 5973 instrument coupled with a HP 6890 (30 m HP 5-MS column, coating 5%-diphenyl-95%-dimethyl-polysiloxane, diameter 0.25 mm, film thickness 0.25 μm) in connection with an autosampler. FTIR spectra were recorded on a Nicolet Impact 400d FTIR-spectrometer using KBr plates. NMR spectra were recorded on a DRX 400 spectrometer (Bruker Instruments Inc., Billerica, MA, USA) using $CHCl_3$ as internal standard. Water contents were determined by Karl-Fischer titration on a 652-KF-Coulometer (Metrohm, Herisau, Switzerland). All reaction mixtures were analyzed by gas chromatography using external calibration with pure compounds. All products were characterized by IR, standard NMR techniques ($^1H$, $^{13}C$, DEPT) and GC/MS. The obtained NMR data matched simulated values.[24]

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