Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Shuji Kondo[a]; Nobuo Nakashima[a]; Kazuichi Tsuda[a]
[a] Nagoya Institute of Technology Gokisocho, Nagoya, Japan

To cite this Article Kondo, Shuji , Nakashima, Nobuo and Tsuda, Kazuichi(1989) 'Preparation of Polymeric Analogs of Tetramethylurea and Their Use as Liquid-Liquid Phase-Transfer Catalysts', Journal of Macromolecular Science, Part A, 26: 10, 1425 — 1435

To link to this Article: DOI: 10.1080/00222338908052060

URL: http://dx.doi.org/10.1080/00222338908052060

J. MACROMOL. SCI.–CHEM., A26(10), pp. 1425-1435 (1989)

PREPARATION OF POLYMERIC ANALOGS OF TETRAMETHYLUREA AND THEIR USE AS LIQUID—LIQUID PHASE-TRANSFER CATALYSTS

SHUJI KONDO,* NOBUO NAKASHIMA, and KAZUICHI TSUDA

Nagoya Institute of Technology
Gokisocho, Showa-ku, Nagoya 466, Japan

ABSTRACT

Polymeric analogs of tetramethylurea were prepared by free-radical polymerization of *N,N,N'*-trimethyl-*N'*-*p*-vinylbenzylurea and copolymerization of this monomer with styrene. These polymers are soluble in toluene and have the ability to extract alkali metal ions such as lithium, sodium, and potassium. Moreover, these polymers act as phase-transfer catalysts for typical S_N2 reactions, although the monomeric analogs tetramethylurea and *N,N,N'*-trimethyl-*N'*-benzylurea do not. A plausible mechanism for these catalytic reactions is proposed.

INTRODUCTION

Various kinds of phase-transfer catalysts have been discovered recently, and they have stimulated much development in organic synthesis [1-4]. Among them, onium salts, such as ammonium and phosphonium salts, crown ethers, cryptands, and linear polyethers are known as effective catalysts. Anchoring these catalysts to insoluble polymers has also been investigated because of the easy isolation of product and recovery of catalyst [5-10]. However, the catalytic activity of these polymers is generally lower than that of the corresponding soluble phase-transfer catalysts.

In recent articles we reported that soluble polystyrenes carrying active sites of dipolar aprotic solvents such as *N,N*-dimethylformamide [11], *N,N*-dimethylacetamide [12], dimethylsulfoxide [13], and sulfolane [14] serve as phase-transfer catalysts although the corresponding monomeric analogs are ineffective. In addition, these polymers have extraction ability for alkali metal picrates regardless of the alkali metal species. On the other hand, Barker and Caruso previously revealed that tetramethylurea, used as a dipolar aprotic solvent, has solvation selectivity toward alkali metal ions [15]. These findings prompted us to examine the activity of polymers containing the tetramethylurea moiety in phase-transfer reactions.

This article describes the preparation of polymers and their activity in phase-transfer reactions. We further propose a plausible mechanism for these catalytic reactions.

EXPERIMENTAL

Materials

p-Chloromethylstyrene was prepared by the method described previously [16]. *N,N,N'*-Trimethyl-*N'*-benzylurea was prepared by the method of Kessler and Kalinowski [17]. Styrene, *n*-octyl bromide, benzyl bromide, *n*-octyl methanesulfonate, phenol, thiophenol, and solvents were used after distillation. Azobisisobutyronitrile (AIBN) initiator was recrystallized from methanol. Benzyltriethylammonium chloride, tetrabutylammonium hydrogen sulfate, and 18-crown-6 phase transfer catalysts as well as other reagents were obtained commercially and used without further purification.

Preparation of *N,N,N'*-Trimethyl-*N'*-*p*-vinylbenzylurea (*TMVU*)

To a slurry of 2.6 g (65 mmol) sodium hydride (~60%, oil suspension) and 200 mL *N,N*-dimethylformamide (DMF) was added 6.2 g (60 mmol) trimethylurea, and the mixture was stirred under nitrogen at room temperature for 2 h. To this mixture, 7.7 g (50 mmol) *p*-chloromethylstyrene was added dropwise over 30 min at 0°C. After stirring overnight at room temperature, it was filtered. The filtrate was poured into 1 L water and extracted three times with 80 mL methylene chloride, and dried over sodium sulfate. The oily residue obtained after filtration and solvent removal was separated by silica gel column chromatography (Wakogel C-200) with methylene chloride as eluent to give 6.7 g (61%) *N,N,N'*-trimethyl-*N'*-*p*-vinylbenzylurea as a colorless liquid. NMR (in $CDCl_3$) $\delta = 2.72$ (s, 3H), 2.84 (s, 6H), 4.35 (s, 2H), 5.23 (d, 1H), 5.73 (d, 1H), 6.76 (dd, 1H), and 7.31 ppm (d, 4H) IR: $\nu_{C=C} = 920$ and $1000\ cm^{-1}$, $\nu_{C=O} = 1650\ cm^{-1}$.

Analysis. Calculated for $C_{13}H_{18}N_2O$: C, 71.63; H, 8.31; N, 12.83%. Found: C, 71.09; H, 8.10; N, 12.47%.

Polymerization Procedure

Polymerization was carried out in a sealed tube with shaking in a thermostat. The charging of the reagents into an ampule and its sealing were done as reported previously [16].

After polymerization for a given time, the tube was opened and its content was poured into a large amount of methanol to precipitate the polymer formed. The resulting polymer was purified by reprecipitation from benzene into petroleum ether. The precipitation procedure was repeated several times, and the conversion was calculated from the nitrogen analysis.

Reaction of *n*-Octyl Bromide with Several Nucleophiles

In a typical run, a toluene solution (1 mL) of *n*-octyl bromide (0.32 g), a solution of sodium iodide (2.57 g) in water (5 mL), and catalyst 3a (65 mg) (see Scheme 1) were placed in a test tube. The tube was heated without shaking in an oil bath at 100°C for 20 h, and then the reaction mixture was poured into petroleum ether. The precipitated solid was filtered off, and the filtrate was analyzed by gas chromatography. The yield of *n*-octyl iodide was 83%. Other reactions were carried out in the essentially same way.

Reaction of Phenoxide with Benzyl Bromide

This reaction was carried out as described previously [13].

Reaction Rate Measurement

A typical experiment was carried out as follows: A 30 mL round-bottomed flask, equipped with reflux condenser, was charged with 4.0 *M* potassium iodide in water (15 mL), cyclohexylbenzene (0.20 g) as internal standard, and 0.5 mmol (109 mg) of 3a. The mixture was heated at 100°C. Then 1.65 *M n*-octyl methanesulfonate in toluene (1.67 mL) was added at zero time. The reaction was followed by GLC analysis (Silicone SE-30, 20% over Celite 545 at 150°C), and the results were corrected by calibration with standard mixtures. The pseudo-first-order rate constants (k_{obs}) were obtained by plotting the logarithm of substrate concentration vs time and determining the slope of the straight line.

Extraction

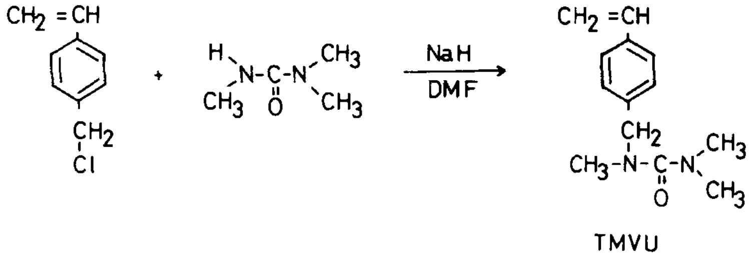
The extraction ability was evaluated by a modification of the method reported by Pedersen [18], Frensdorff [19], and Smid [20]. To 20 mL of a toluene solution of the polymer containing 0.63 mmol urea units was added 5 mL of an aqueous picric acid solution (50 μmol/L) containing excess metal hydroxide (10 mmol/L). The mixture was stirred magnetically for 3 h at 20°C. After separating, the aqueous solution was analyzed by means of the picrate absorption at 355 nm.

Measurements

UV spectra were recorded with a Hitachi 124 spectrometer. IR spectra were measured with a Jasco IR-2 spectrophotometer. NMR spectra were recorded with a Hitachi R-20B spectrometer using tetramethylsilane as internal standard. Gas chromatography (Ohkura 802) was used for separation and yield determination. The intrinsic viscosity was determined in DMF at 30°C.

RESULTS AND DISCUSSION

To study the relationship between structure and catalytic activity, polymers with well-defined structure are desirable. Thus we attempted to prepare a polymer containing the tetramethylurea moiety by polymerization of a new monomer, *N,N,N*′-trimethyl-*N*′-*p*-vinylbenzylurea (TMVU). TMVU was prepared by the reaction of *p*-chloromethylstyrene with trimethylurea in the presence of sodium hydride:



(1)

TMVU polymerized smoothly under free-radical conditions to give a white solid with an intrinsic viscosity of 0.15.

In order to clarify the reactivity of TMVU for radical copolymerization,

TABLE 1. Copolymerization of TMVU (M_1) with Styrene (M_2)[a]

M_1[b]	Conversion, %	N, %	m_1[c]
0.15	4.2	3.06	0.14
0.30	4.7	5.17	0.26
0.40	5.6	6.55	0.33
0.50	6.5	7.95	0.44
0.60	6.7	8.76	0.53
0.70	8.0	9.70	0.61
0.85	9.3	11.16	0.76

[a] $[M_1] + [M_2] = 1.0$ mol/L; [AIBN] = 10 mmol/L; solvent, benzene; 60°C; time, 2 h.

[b] Mole fraction of TMVU in monomer mixture.

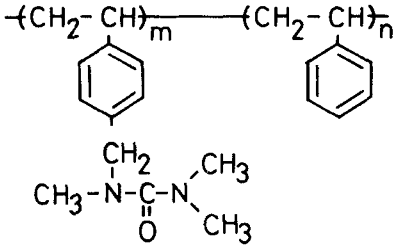
[c] Mole fraction of TMVU in copolymer.

copolymerization with styrene was carried out. As can be seen from Table 1, the mole fraction of TMVU in the monomer mixture (M_1) is quite similar to that in the copolymer (m_1). The monomer reactivity ratios were computed by the Fineman-Ross method as $r_{TMVU} = 0.71$ and $r_{St} = 1.15$. From these values the resonance-stabilized factor Q and electrical factor e of TMVU were calculated as $Q = 0.61$ and $e = -0.35$.

Based on the monomer reactivity ratios, several copolymers with different compositions (3a-d) were prepated as catalysts (see Scheme 1).

These polymers are soluble in benzene, toluene, and methylene chloride, but insoluble in water. If these polymers act as phase-transfer catalysts, they should be able to extract alkali metal ions from an aqueous phase. Therefore, the extraction ability of the polymers was examined (Table 2). All polymeric ureas employed here extract alkali metal ions such as Li^+, Na^+, and K^+, but monomeric compounds such as tetramethylurea (1) and *N,N,N′*-trimethyl-*N′*-benzylurea (2) do not do so to any detectable degree. Furthermore, the extraction ability increases with increasing active site density in the polymer.

These results can be explained by a mechanism involving chelation of a metal ion with several urea groups. Similar phenomena have been observed in polymeric analogs of dipolar aprotic solvents, such as dimethylsulfoxide, sulfolane, and hexamethylphosphoramide [13, 14, 21]. Though K^+ seems



3

Polymer	n/m	[η]
3a	0	0.15
3b	0.4	0.11
3c	1.0	0.13
3d	2.1	0.18

SCHEME 1.

TABLE 2. Extraction of Picrate Salts by Ureas

	Picrate salt extracted, %		
Catalyst	Li^+	Na^+	K^+
1[a]	0	0	0
2[b]	0	0	0
3a	9	11	13
3b	7	8	10
3c	5	7	6
3d	2	4	4

[a] Tetramethylurea.

[b] *N*,*N*,*N*′-Trimethyl-*N*′-benzylurea.

to be extracted to a somewhat higher degree than Li^+ and Na^+, a clear selectivity with respect to alkali metal ions was not found.

The catalytic activity was tested for the reaction of *n*-octyl bromide with sodium iodide in a toluene-water two-phase system (Table 3).

$$n\text{-}C_8H_{17}Br + NaI \xrightarrow[C_6H_5CH_3-H_2O]{Cat.} n\text{-}C_8H_{17}I + NaBr \qquad (2)$$

This reaction takes place in the presence of 3a, but is not catalyzed by the monomeric analogs, 1 and 2. Thus the catalytic activity of the polymeric urea is superior to that of its monomeric analogs.

In addition, the activity of 3a is comparable to that of the commercial phase-transfer catalyst, benzyltriethylammonium chloride (BTEAC), for the substitution reaction of *n*-octyl bromide with potassium thiocyanate, but is lower than that of tetrabutylammonium hydrogen sulfate (TBAHS) and 18-crown-6. Catalyst 3a was recovered by reprecipitation with petroleum ether and subsequent filtration. The catalytic activity of reused polymer was reduced slightly. This polymer is also effective as a catalyst for the reaction of *n*-octyl bromide with lithium iodide, potassium iodide, sodium cyanide, sodium thiophenoxide, and sodium thiocyanate.

Moreover Table 3 shows that catalytic activity depends markedly on the composition of copolymer and runs parallel to extraction ability. Similar observations have been reported for polymeric phosphoramides as phase-transfer catalysts [21]. Previously, we concluded that the most important factors for the catalytic activity of polymeric analogs of *N,N*-dimethylacetamide [12] and dimethylsulfoxide [13] are the extraction ability for alkali metal ions and desolvation of anions derived from the lipophilicity around the active sites. In the present case, the lipophilicity was not found to be very important for the relation between activity and composition ratio. This result may be explained by the assumption that sufficient lipophilicity is already conferred by the alkyl groups around the active sites in the polymeric tetramethylureas.

It is well known that the C/O alkylation ratio of phenol is related to the specific solvation of phenoxide in the medium, i.e., water favors C-alkylation whereas toluene leads to the O-alkylation product [22]. In order to obtain information about the reaction phase, we examined the reaction of benzyl bromide with sodium phenoxide with 3a as catalyst, and the O-alkylation product benzyl phenyl ether was obtained exclusively. Accordingly, it was concluded this catalytic reaction occurs in the organic phase.

$$C_6H_5CH_2Br + C_6H_5O^- \xrightarrow[C_6H_5CH_3-H_2O]{3a} C_6H_5OCH_2C_6H_5 \qquad (3)$$

TABLE 3. Reaction of *n*-Octyl Bromide with Several Nucleophilic Reagents under Phase-Transfer Conditions at 100°C for 20 h[a]

Reagents	Catalyst	Yield, %	Product
NaI	–	Trace	n-$C_8H_{17}I$
NaI	1	Trace	n-$C_8H_{17}I$
NaI	2	Trace	n-$C_8H_{17}I$
NaI	3a	83	n-$C_8H_{17}I$
NaI	3b	52	n-$C_8H_{17}I$
NaI	3c	23	n-$C_8H_{17}I$
NaI	3d	10	n-$C_8H_{17}I$
NaI	3a[b]	78	n-$C_8H_{17}I$
LiI	3a	81	n-$C_8H_{17}I$
KI	3a	63	n-$C_8H_{17}I$
KCN	3a	95	n-$C_8H_{17}CN$
$NaSC_6H_5$	3a	100	n-$C_8H_{17}SC_6H_5$
NaSCN	3a	78	n-$C_8H_{17}SCN$
KSCN	3a	72	n-$C_8H_{17}SCN$
KSCN	BTEAC[c]	69	n-$C_8H_{17}SCN$
KSCN	TBAHS[d]	98	n-$C_8H_{17}SCN$
KSCN	18-Crown-6	98	n-$C_8H_{17}SCN$

[a] [n-$C_8H_{17}Br$] = 1.65 mol/L (in toluene), 1 mL; [LiI, NaI, KI] = 4.0 mol/L (in H_2O), 5 mL; [KCN, NaSCN, KSCN] = 8.0 mol/L (in H_2O), 5 mL; [$NaSC_6H_5$] = 2.0 mol/L (in H_2O), 5 mL; [catalyst] = 0.3 mmol based on urea unit.

[b] Reused catalyst.

[c] Benzyltriethylammonium chloride.

[d] Tetrabutylammonium hydrogen sulfate.

TABLE 4. Reaction of *n*-Octyl Methanesulfonate with Sodium Halides under Phase-Transfer Conditions

NaX	k_{obs}, s^{-1}
NaCl	2.8×10^{-6}
NaBr	9.1×10^{-6}
NaI	3.8×10^{-5}

Further information about the reaction phase was obtained from the reaction of *n*-octyl methanesulfonate with sodium halides. The dependence of the reaction rate on the nucleophile was estimated by measuring the pseudo-first-order rate constants (Table 4).

$$n\text{-}C_8H_{17}OSO_2CH_3 + NaX \xrightarrow[C_6H_5CH_3-H_2O]{3a} n\text{-}C_8H_{17}X + CH_3SO_3Na \tag{4}$$

$$X = Cl, Br, I$$

If this reaction occurs in a nonaqueous phase, the reactivity of the halides would decrease in the order $Cl^- > Br^- > I^-$ [23]. However, the observed results were the reverse of the above order, suggesting the existence of water in the reaction phase [23]. From the results of phenoxide substitution and reactivity of halides as nucleophiles, we deduce that the catalytic reaction occurs in the organic phase, which contains a small amount of water.

The observed data, as a whole, indicate that phase-transfer reactions catalyzed by polymeric ureas follow a mechanism in which the oxygen atoms of the urea groups in the polymer coordinate to alkali metal ions at the interface, resulting in the transfer of the cation together with the counter-anion from the aqueous phase to the organic phase, where the anion attacks the substrate.

ACKNOWLEDGMENT

This work was partially supported by a Grant-in-Aid for Scientific Research No. 63550680 from the Japan Ministry of Education, Science and Culture.

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Received July 19, 1988
Revision received October 15, 1988