

# NOTE

## Crosslinking of Chlorinated Poly(Dimethylsiloxanes) with Thiol Compounds

Crosslinking of polysiloxanes is of practical interest. High-temperature peroxide-catalyzed crosslinking, platinum-catalyzed hydrosilylation, and moisture-hydrolysis curing are known to be typical examples for silicone vulcanization.<sup>1</sup> Those methods have been already established as industrial processes for silicone elastomers.

Halogen-containing polymers, such as poly(vinyl chloride) (PVC),<sup>2-11</sup> poly(epichlorohydrin) (CHR),<sup>12-16</sup> polychloroprene (CR),<sup>17</sup> and fluoro rubbers (FR),<sup>18,19</sup> were reported to crosslink with thiol and amine compounds in the presence of acid acceptors (metal oxides and so on) mainly by Nakamura and Mori. Furthermore, this technology is applied for industrial crosslinking of these polymers. In this process, the crosslinking is based upon nucleophilic substitution reactions on C-halogen bonds by multifunctional reagents and, therefore, nucleophilicity of the reagents plays an important role for effective crosslinking. This evidently suggests that multifunctional thiol compounds like triazine thiols constitute excellent reagents for cocrosslinking between different types of polymers. Nakamura and Mori intensively studied cocrosslinking of some polymer blend systems such as polyethylene-PVC,<sup>20</sup> nitrile rubber-PVC,<sup>21</sup> PVC-CR,<sup>22</sup> and FR-CHR<sup>18,19</sup> using the thiol compounds.

For polysiloxanes, it is also expected that the thiol and amino compounds will constitute a new type of crosslinking system when their chlorinated derivatives [chlorinated poly(dimethylsiloxanes) (C-PDMSs)] are applied. The chloromethyl groups on C-PDMSs were already found to be readily displaced by diethyldithiocarbamate anion,<sup>23,24</sup> indicating that the thiolate anions possessed high nucleophilic reactivity toward C-PDMSs.

In this work, some thiol and amine compounds were examined for crosslinking of C-PDMSs derived from photochlorination of poly(dimethylsiloxanes) and ring-opening polymerization of a chlorine-containing cyclo-tetrasiloxane.

### EXPERIMENTAL

#### Materials

Two kinds of C-PDMSs were prepared by photochlorination of poly(dimethylsiloxane) (Shin-Etsu, KE-76,

1,000,000 cs of viscosity)<sup>25</sup> and ring-opening polymerization of chloromethylheptamethylcyclotetrasiloxane.<sup>26</sup> Those C-PDMSs are, hereafter, abbreviated as C-PDMS(PC) and C-PDMS(ROP), respectively. Synthesis of bromine-containing C-PDMS (Br-C-PDMS) was described elsewhere.<sup>24</sup>

Commercial 2-*R*-4,6-dithiol-*s*-triazines [*R*-dibutylamino- (DB) and anilino- (AN), Sankyo Kasei Co.] were recrystallized from benzene. Trithiocyanuric acid (TCA, Tokyo Chemical Ind.) was used without further purification. Monosodium salt of DB (DB-Na) was prepared by an equimolar reaction between DB and sodium hydroxide.

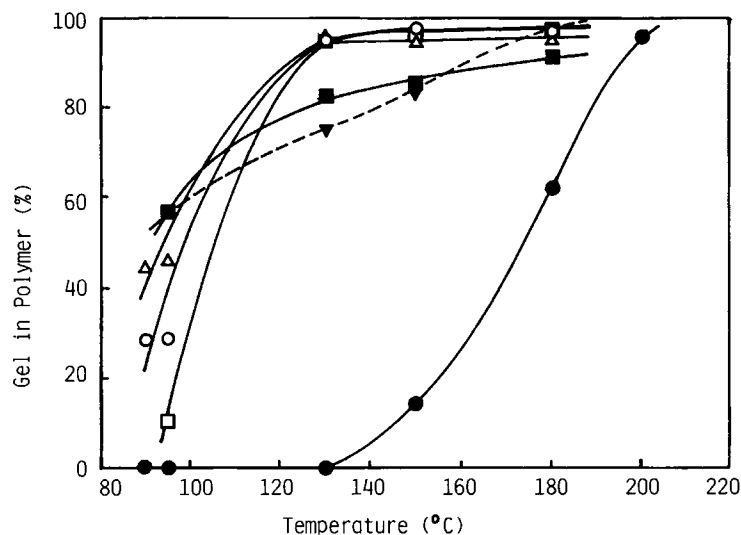
1,6-Hexamethylenediamine (HMDA, Wako Pure Chemical Ind.), triethylenetetramine (TETA, Katayama Chemical Ind.), *p,p'*-diaminodiphenylmethane (DDM, Katayama Chemical Ind.), benzoguanamine (BG), ethylenethiourea (ETU, Nakarai Chemicals), and 2,5-dimercapto-1,3,4-thiodiazole (DMT, Tokyo Chemical Ind.) were used as received. Commercial melamine (Mel) was recrystallized from water. Magnesium oxide (Ishizu Pharmaceutical Co.) as an acid acceptor was used as received.

#### Crosslinking of C-PDMSs

C-PDMS and additives were blended manually in an agate mortar by the help of solvent, followed by evaporation, or by laboratory mill. The blended materials were coated on slide glasses (76 × 26 × 1 mm, Matsunami Glass Ind.). The slide glasses were then placed in an oven adjusted at given temperatures to allow curing of C-PDMSs.

#### Analysis

The contents of chloromethyl (ClCH<sub>2</sub>-) and bromomethyl groups (BrCH<sub>2</sub>-) were determined by [<sup>1</sup>H] nuclear magnetic resonance (NMR) spectra using a Hitachi NMR spectrometer R-24 and a JEOL JNM FX90 FT NMR spectrometer in CCl<sub>4</sub> and CDCl<sub>3</sub>, respectively, at 30°C. Intrinsic viscosity of C-PDMSs was measured at 25°C with a Ubbelohde viscometer using toluene as a solvent. Degree of crosslinking, i.e., gel % in C-PDMS, was estimated by means of Soxhlet extraction of the crosslinked C-PDMS/slide glasses in toluene.

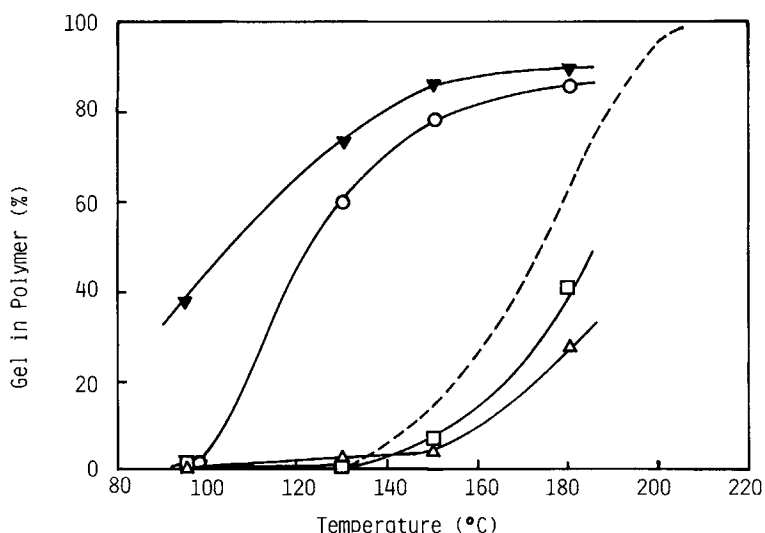


**Figure 1** Crosslinking of C-PDMS(PC) with several reagents. C-PDMS(PC):  $\text{ClCH}_2$ -5.3 mol %,  $[\eta] = 0.59$  dL/g. Compounding: C-PDMS(PC), 100 parts; crosslinking agent, 10 parts; MgO, 2 parts. Reaction time: 1 h. (—○—) DB + MgO; (—△—) DB-Na + MgO; (—□—) DB; (—■—) DB-Na; (—▼—) HMDA + MgO; (—●—) none.

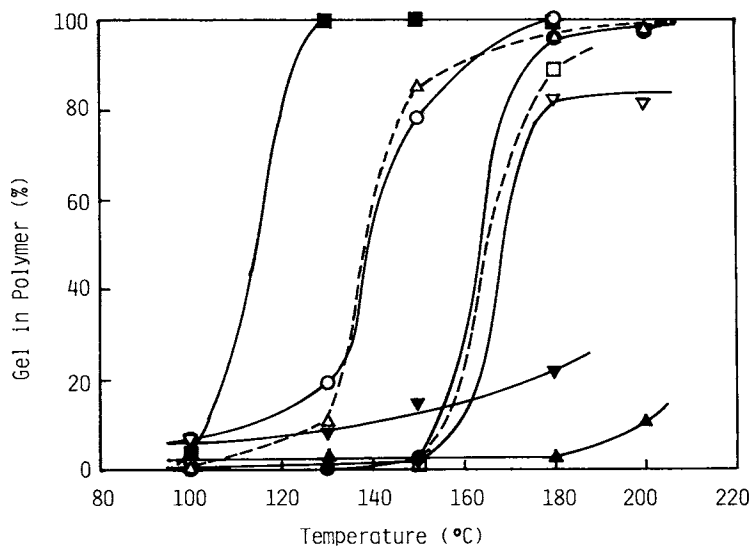
## RESULTS AND DISCUSSION

As already reported,<sup>25</sup> C-PDMS(PC) obtained by photochlorination contained not only chloromethyl group but also a small amount of dichloromethyl group ( $\text{Cl}_2\text{CH}-$ ) in their polymers when the chlorine content exceeds ca. 5 wt %. The C-PDMS(PC) sample used here was estimated to have chloromethyl contents of 5–6 mol %, in which the

dichloromethyl group was hardly detected by means of NMR spectroscopy. Therefore, the C-PDMS(PC) used in this experiment is almost regarded as poly(dimethylsiloxane) containing only the chloromethyl group, similar to the C-PDMS(ROP) derived from ring-opening polymerization of a chloromethyl-containing cyclo-tetrasiloxane. However, low sensitivity of the group in proton NMR analysis could not deny a possibility that



**Figure 2** Crosslinking of C-PDMS(PC) with several reagents at various temperatures. C-PDMS(PC):  $\text{ClCH}_2$ -5.7 mol %,  $[\eta] = 0.78$  dL/g. Compounding: C-PDMS(PC), 100 parts; crosslinking agent, 10 parts; MgO, 2 parts. Reaction time: 1 h. (—▼—) TETA + MgO; (—○—) DDM + MgO; (—□—) Mel + MgO; (—△—) BG + MgO; (---) none.



**Figure 3** Crosslinking of C-PDMS (ROP) with several reagents at various temperatures. C-PDMS (ROP):  $\text{ClCH}_2$ - 6.6 mol %,  $[\eta] = 0.39$  dL/g. Compounding: C-PDMS (ROP), 100 parts; crosslinking agent, 10 parts; MgO, 2 parts. Reaction time: 1 h. (—■—) BD + MgO; (---△---) TETA + MgO; (---○---) BD-Na + MgO; (—●—) ETU + MgO; (---□---) AN + MgO; (—▽—) DDM + MgO; (—▼—) TCA + MgO; (—▲—) DMT + MgO.

trace amounts of the dichloromethyl group is introduced into C-PDMS(PC)s.

Figures 1, 2, and 3 show curing behavior of C-PDMS(PC) and C-PDMS(ROP) with several crosslinking agents as a function of reaction temperature.

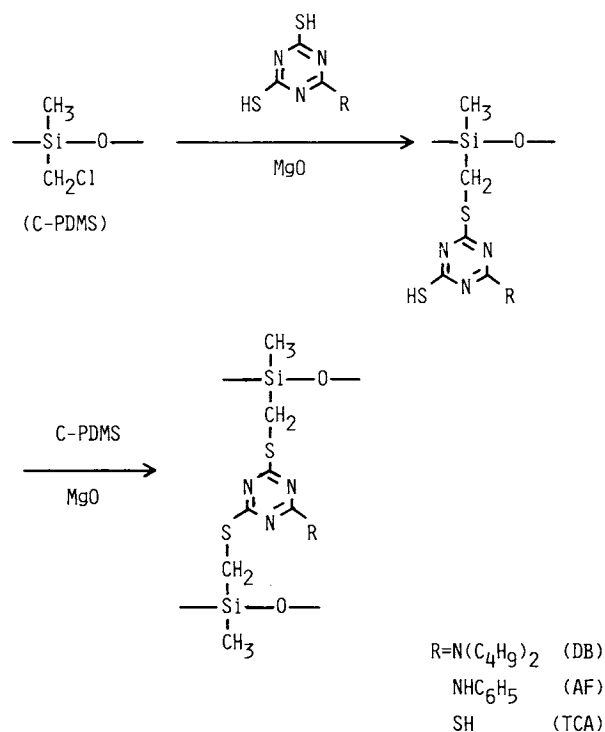
These figures suggest that amines and triazine thiols are effective for crosslinking, although C-PDMS(PC)s themselves are labile to cure at higher than 150°C. In particular, triazine thiols, i.e., DB and DB-Na, were found to function as active crosslinking agents, as assessed from high reaction rate and lack of oxidative degradation, i.e., discoloration of their products. The crosslinking proceeded with formation of triazine thiolate linkages between the chloromethyl groups via triazine thiolate branching in the first step (see scheme 1), similarly to the crosslinking mechanism for CHR<sup>12,14</sup> and PVC<sup>2,3</sup> proposed by Nakamura and Mori. In these reactions, MgO played an important role as an acid acceptor.<sup>2,12</sup> A small difference in crosslinking behavior was observed between two kinds of C-PDMSs at a relatively low temperature region (ca. 100°C).

The crosslinking rates of C-PDMSs roughly estimated from Figures 1, 2, and 3 tend to increase in the following order: TCA < AN < DB for triazine thiols and DDM < HMDA < TETA for amines. Basicity of thiolate and amine reagents is an important factor in the control of their nucleophilic crosslinking performance, as revealed from the first dissociation constants,  $\text{pK}_a = 4.1, 5.5,$  and  $6.5$  for DB, AN, and TCA, respectively.<sup>27</sup>

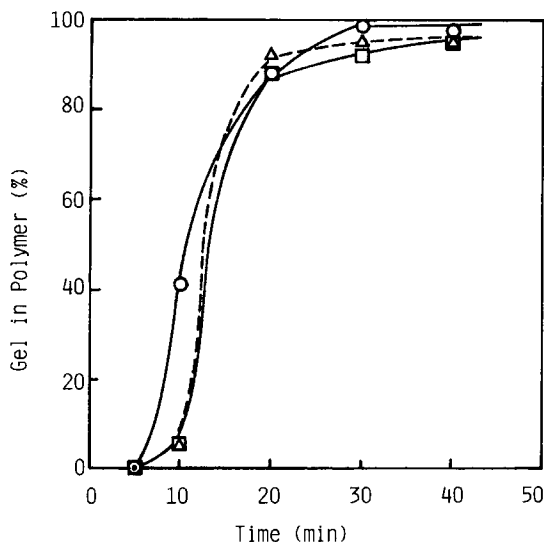
Figure 4 illustrates an effect of polymer viscosity of C-PDMSs on crosslinking. The rate of gel formation was

found to be almost same in these regions of the polymer viscosity, namely, molecular weight.

Figure 5 shows DB concentration dependence of cross-



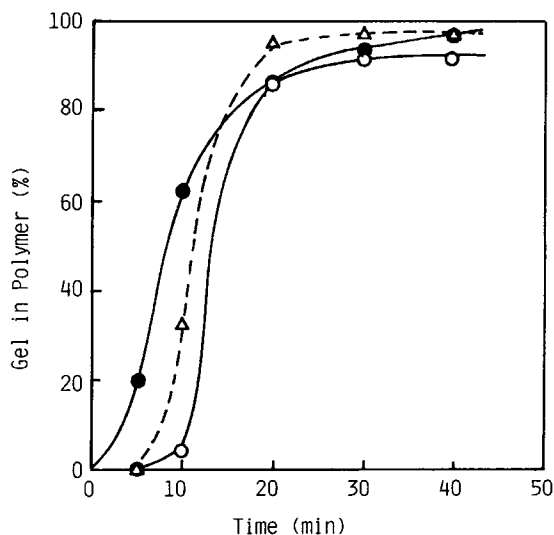
**Scheme 1** Crosslinking of C-PDMS.



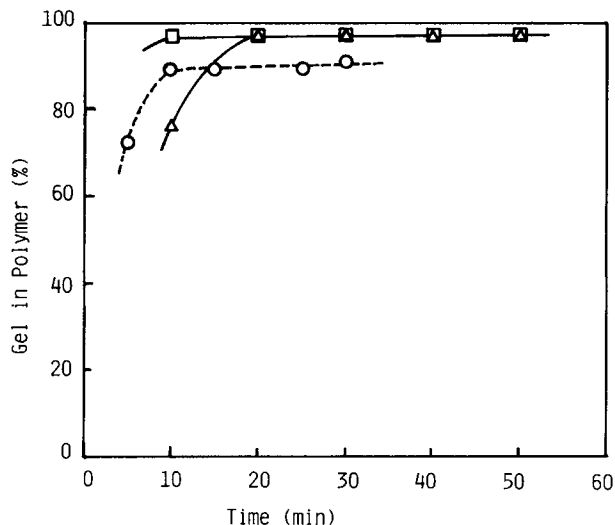
**Figure 4** Dependence of polymer viscosity on crosslinking of C-PDMS(ROP) with DB/MgO system at 150°C. C-PDMS(ROP):  $\text{ClCH}_2$ - 12.5 mol %,  $[\eta]$  = variable. Compounding: C-PDMS(ROP), 100 parts; DB, 2 parts; MgO, 2 parts. (—○—) 0.81; (---△---) 0.53; (—□—) 0.39 dL/g.

linking of C-PDMSs. This evidently indicates that the crosslinking rates increase with the DB concentration in the initial reaction region.

A bromine-containing C-PDMS, i.e., Br-C-PDMS, was found to cure with the same crosslinking agent at 180°C,



**Figure 5** Concentration dependence of DB on crosslinking of C-PDMS(ROP) with DB/MgO system at 150°C. C-PDMS(ROP):  $\text{ClCH}_2$ - 12.5 mol %,  $[\eta]$  = 0.53 dL/g. Compounding: C-PDMS(ROP), 100 parts; DB, variable; MgO, 2 parts. (—○—) 1; (---△---) 3; (—●—) 7 parts.



**Figure 6** Crosslinking of C-PDMS(PC) and Br-C-PDMS with DB/MgO system. C-PDMS(PC):  $\text{ClCH}_2$ - 5.3 mol %,  $[\eta]$  = 0.59 dL/g. Br-C-PDMS:  $\text{ClCH}_2$ - 3.3 mol %,  $\text{BrCH}_2$ - 4.1 mol %,  $[\eta]$  = 0.21 dL/g. Compounding: C-PDMS(PC) or Br-C-PDMS, 100 parts; DB, 10 parts; MgO, 2 parts. (—□—) C-PDMS(PC), 180°C; (—△—) C-PDMS(PC), 130°C; (---○---) Br-C-PDMS, 180°C.

as shown in Figure 6, although a slight difference in the ultimate degree of crosslinking was observed in comparison with C-PDMSs.

Thus, the chloromethyl side groups on polysiloxane backbones were reactive toward several nucleophiles, such as amine and thiol compounds, to afford their crosslinked products, similarly to poly(epichlorohydrin) having chloromethyl side groups.<sup>12-16</sup> In particular, triazine thiols in the presence of magnesium oxide were confirmed to be effective for crosslinking because of their high nucleophilicity. This crosslinking system is of industrial interest as a new silicone vulcanization method.

Also, thermal crosslinking of C-PDMS/halogen-containing polymer blends using the same reagents is expected to become a promising method to prepare silicone-modified polymer blends. A study of typical combination of C-PDMS with PVC for crosslinking is in progress and will be reported soon.<sup>28</sup>

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Received May 22, 1991

Accepted December 13, 1991