

Formation of a Bicontinuous Structure Membrane of Polyvinylidene Fluoride in Diphenyl Carbonate Diluent Via Thermally Induced Phase Separation

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ABSTRACT: Diphenyl carbonate was used as a diluent to prepare microporous polyvinylidene fluoride (PVDF) membrane via thermally induced phase-separation method. The liquid–liquid phase-separation phenomenon was found in PVDF/diphenyl carbonate system during the thermally induced phase-separation process. The monotectic point of this system appeared at a high polymer concentration approximately 56 wt %. This suggested that PVDF membrane with a bicontinuous or cellular structure could be obtained when the PVDF concentration was less than this point value. The effects of polymer concentration and quenching temperature on the membrane structure, porosity, and tensile strength were also investi-

gated. The results showed that low polymer concentration and high quenching temperature led to a large pore size membrane. The tensile strength of the membrane increased with increase in the polymer concentration, but the porosity of the membrane decreased. On condition that the PVDF concentration was higher than 60 wt %, only polymer crystallization occurred and a typical compact spherulitic structure was obtained. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1523–1528, 2009

Key words: polyvinylidene fluoride; membrane; thermally induced phase separation; diphenyl carbonate; monotectic point

INTRODUCTION

Polyvinylidene fluoride (PVDF) is an acid resistant, heat steady, semicrystalline polymer widely used to produce microporous membrane for water treatment process, such as microfiltration and ultrafiltration.^{1,2} More and more attention is being paid to the preparation of microporous PVDF membrane via thermally induced phase-separation (TIPS) method due to their excellent physical and chemical properties.^{3–14} Such membranes were mainly prepared from binary systems of PVDF in different diluents namely cyclohexanone (CO),³ γ -butyrolactone,^{3,4} propylene carbonate,^{3,5} carbitol acetate,³ dimethyl phthalate,^{6,7} dibutyl phthalate,^{7–11} glyceryl triacetate,^{12,13} and sulfolane.¹⁴ Most of the PVDF/diluent systems underwent solid–liquid phase separation (polymer crystallization) and

got the fuzzy spherulitic structure at the PVDF concentration studied.

In our preceding work,¹⁵ the application of diphenyl ketone (DPK) as a new diluent for the preparation of microporous PVDF membrane via TIPS method was discussed. The phenomenon of liquid–liquid (L-L) phase separation was found in this system and a bicontinuous structure was obtained when the temperature was decreasing and the PVDF concentration was less than 30 wt %. However, the resulting membranes presented unsatisfactory mechanical properties due to the low PVDF concentration used. Generally, it was preferred that L-L phase separation could occur during the TIPS process in polymer/diluent system at polymer concentration more than 30 wt % and then the resulting microporous polymer membrane could present both good structure and excellent mechanical properties.¹⁶ In TIPS process, the diluent played an important role in controlling the phase-separation mechanism of polymer/diluent system and the resulting membrane structure. The compatibility of polymer and diluent directly reflected thermodynamic properties such as the binodal curve and crystallization temperature. As the compatibility became lower, the binodal curve was shifted to the higher temperature,

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whereas the crystallization temperature was less influenced by the compatibility.¹⁷ This meant that the monotectic point (the intersection of the binodal curve and the crystallization temperature curve) could be extended to higher polymer concentration in the case of lower compatibility.

In this work, a novel diluent of diphenyl carbonate (DPC) was used to prepare PVDF membranes by TIPS method, which has several advantages, such as nontoxicity, low volatility, and good thermal stability. The monotectic point of PVDF/DPC system was extended to approximately 56 wt % and a bicontinuous or cellular structure was obtained in PVDF membrane. Moreover, how the polymer concentration and quenching temperature affected the membrane structure, porosity, and tensile strength were also systematically studied on the basis of phase diagram.

EXPERIMENTAL

Materials

PVDF ($M_w = 370\,000$, $M_w/M_n = 2.5$) was supplied by CMDIC XIAMEN (China). Two solvents were used as the diluent, including DPC ($M_w=214.22$, $T_b = 575.15$ K) and diphenyl methane (DPM, $M_w=168.24$, $T_b = 534.15$ K). All chemicals were analytical graded and used without further purification.

Phase diagram determination

A homogeneous solid polymer/diluent sample was prepared with a previously described method.¹⁵ A small piece of the solid sample was sandwiched between a pair of glass microscope coverslips with silicone rubber around to limit diluent evaporation during the experiment. It was then placed on a hot stage (Linkam THMS 600) at 493 K for 5 min, after that the sample was cooled to 373 K at a constant rate of 10 K/min. The temperature of the stage was manipulated by a Linksys32 controller. We determined cloud points visually by noting the appearance of turbidity under an optical microscopy (Olympus BX51).

The dynamic crystallization temperatures were determined by differential scanning calorimetry (TA Q200). The sample was first heated to 493 K with a heating rate of 10 K/min. After keeping at this temperature for 5 min, it was cooled to 313 K with a cooling rate of 10 K/min. The peak crystallization temperature was considered as the crystallization temperature in the phase diagram.

Membrane preparation and characterization

In the sample quenched in a water bath at different temperatures, the diluent was extracted with ethanol

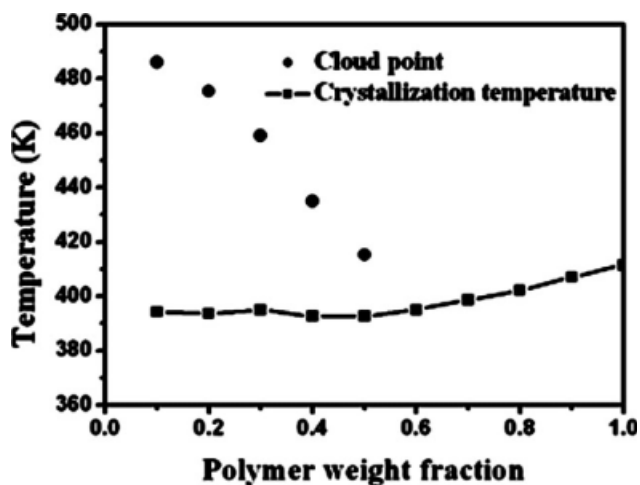


Figure 1 Phase diagram with cloud point temperature and crystallization temperature for PVDF/DPC system at a cooling rate of 10 K/min.

and the microporous PVDF membrane was obtained after the volatilization of ethanol.

Porosity of the resulting microporous PVDF membrane was determined by gravimetric measurements of the difference between dry and fully isobutanol-filled membranes.¹⁸

The resulting microporous PVDF membrane was fractured in liquid nitrogen and coated with platinum. A scanning electron microscope (JEOL JSM7401) with the accelerating voltage set to 1.0 kV was used to examine the cross-section and surface structure of membranes.

The tensile strength of the resulting microporous PVDF membranes was measured by a universal testing machine (Shimadzu AGS-100A) equipped with a 5-kg load cell. Before the test, the membranes with 200 μm thickness were cut into 50 \times 10 mm² strips. The crosshead speed was controlled at 5 mm/min. Average value of the tensile strength was calculated by measuring three samples for each batch of the membranes.

RESULTS AND DISCUSSION

Phase diagram

The phase diagram for PVDF/DPC system is shown in Figure 1, which represents the UCST type L-L phase behavior. As shown in Figure 1, the polymer concentration on the monotectic point of PVDF/DPC system was approximately 56 wt %, which was much higher than that of PVDF/DPK system (<30 wt %).¹⁵ However, in this work, PVDF could not form homogeneous blends with DPM below the boiling temperature of DPM (534 K). This could be explained by different compatibility between the polymer and the diluent molecules, which could be

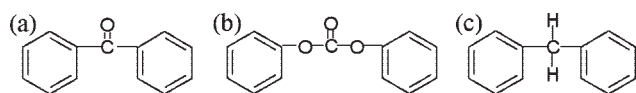


Figure 2 Structure of diluents (a) DPK, (b) DPC, and (c) DPM.

analyzed by the view of the molecular structure of the diluents as follows.

The molecular structures of DPK, DPC, and DPM are shown in Figure 2. It was easy to find that these three diluents had a homologous symmetrical diphenyl structure, but differed in functional groups between diphenyl structure. Basically, the polarity of DPK almost resulted from the stronger electron withdrawing ability of oxygen atom in carbonyl group. In DPC, because of the existence of two oxy-

gen atoms on the two sides of carbonyl group, the electron clouds moved away from oxygen atom contrast to DPK. Therefore, the polarity of DPC was little weaker than DPK leading to the lower compatibility between PVDF and DPC, which resulted in the higher value of the cloud point curve in comparison with that of DPK diluent system. However, the crystallization temperature was less influenced by the compatibility, so that the monotectic point of PVDF/DPC system was successfully extended to higher polymer concentration than PVDF/DPK system. With regards to DPM, the polarity of which was much weaker than DPK and DPC because of its whole symmetrical structure and the methylene group, PVDF could not be compatible with DPM like DPK- and DPC-diluted systems. This suggests that PVDF/DPM system cannot form a

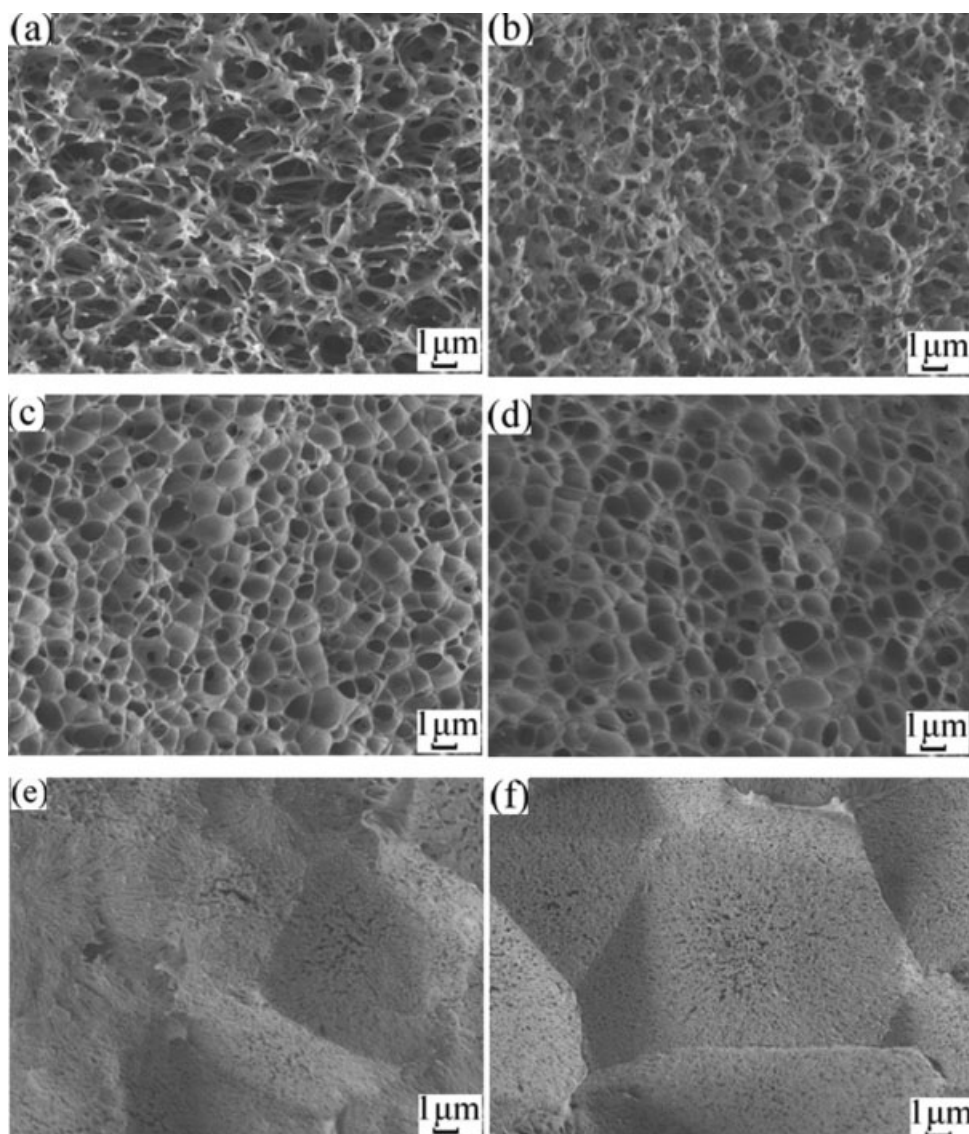


Figure 3 Cross-sectional structure of PVDF membranes prepared by quenching PVDF/DPC solution into ice water: (a) 20 wt %; (b) 30 wt %; (c) 40 wt %; (d) 50 wt %; (e) 60 wt %; and (f) 70 wt %.

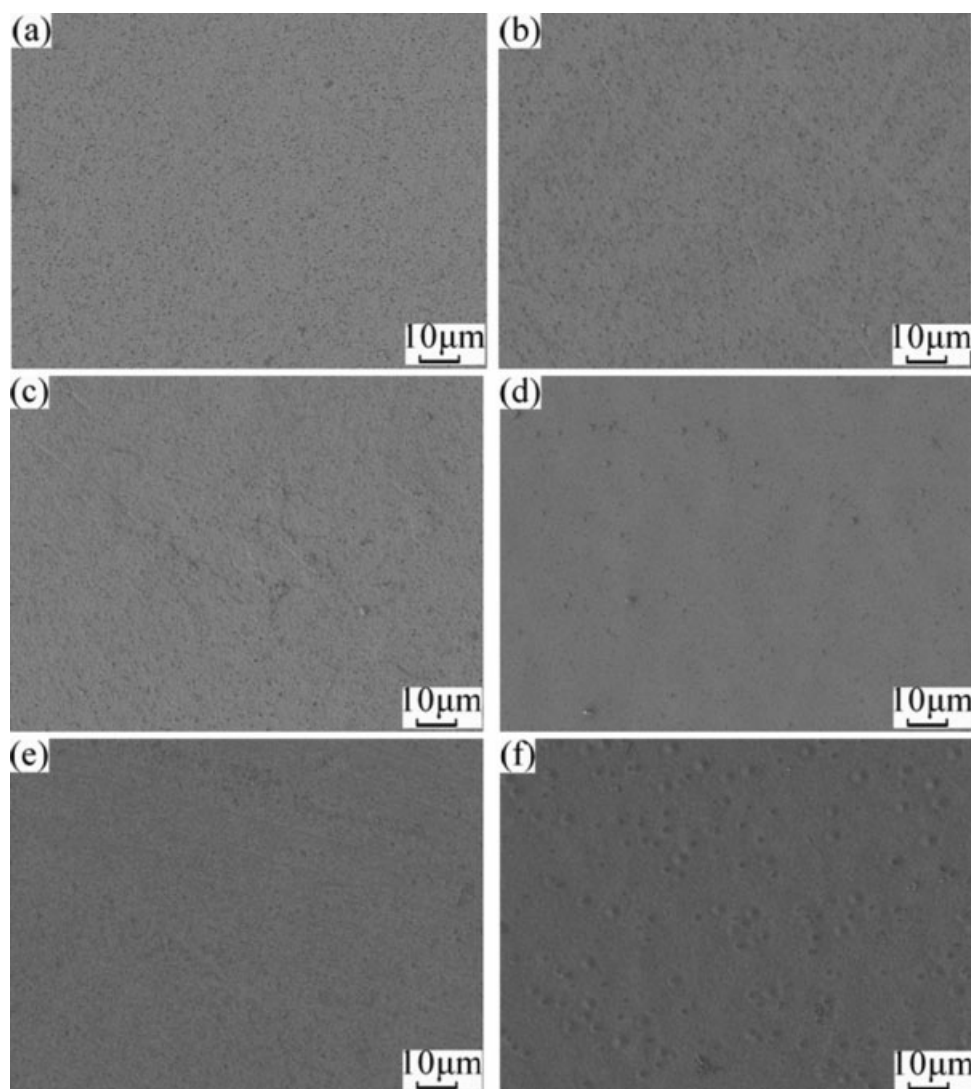


Figure 4 Surface structure of PVDF membranes prepared by quenching PVDF/DPC solution into ice water: (a) 20 wt %; (b) 30 wt %; (c) 40 wt %; (d) 50 wt %; (e) 60 wt %; and (f) 70 wt %.

homogeneous solution at an elevated temperature. So it can be concluded that DPM is not suitable to be a diluent for the preparation of microporous PVDF membrane via TIPS method. As demonstrated earlier, the polarity of diluent plays a significant role on the phase-separation behavior of PVDF/diluent system. It suggests that the compatibility between PVDF and these three dilutes decrease in the order of DPK, DPC, and DPM.

Membrane structure

Figures 3 and 4 show the cross-section and surface structure of the membranes obtained from PVDF/DPC solution with different polymer concentrations when quenched into ice water. These photographs clearly show that the average pore size decreased when the polymer concentration increased. Meanwhile, a clear

bicontinuous or cellular structure was formed at the range of polymer concentration from 20 to 50 wt %. However, a typical compact spherulitic structure was obtained when polymer concentration was higher than 60 wt %. These phenomena could be easy to elucidate by the view of thermodynamics (Fig. 1).

When the polymer concentration increased, the phase-separation mechanism in the TIPS process transformed from L-L phase separation to polymer crystallization.¹⁹ As shown in Figure 1, L-L phase separation could occur before polymer crystallization when the polymer concentrations ranged from 20 to 50 wt %, which lead to the bicontinuous structure [Fig. 3(a,b)] or cellular structure [Fig. 3(c,d)].²⁰ No pore structure was presented in Figure 3(e,f) due to the occurrence of polymer crystallization only when the polymer concentration was higher than the monotectic point value.²¹

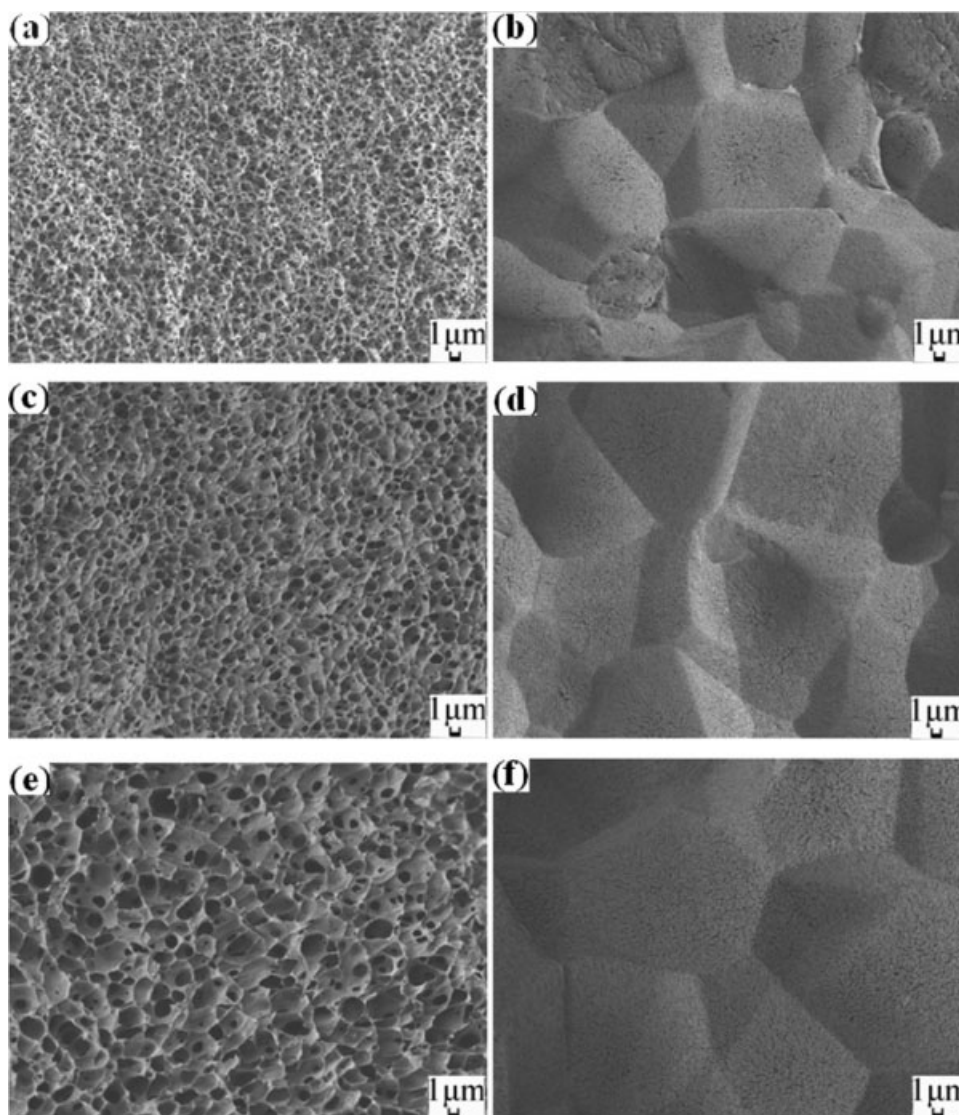


Figure 5 The effect of quenching temperature on the cross-sectional structure of PVDF membranes from PVDF/DPC system, PVDF concentration is 30 wt % at (a) 273 K, (c) 303 K, and (e) 333 K; and PVDF concentration is 70 wt % at (b) 273 K, (d) 303 K, and (f) 333 K.

Figure 5 showed the effect of quenching temperature on the cross-sectional structure of PVDF membranes at the polymer concentration of 30 and 70 wt %. The specific heat capacity of water is so large that the cooling rate of water with different temperatures may differ greatly. At polymer concentration of 30 wt %, the pore size increased with the increase of the quenching temperature due to longer growth time of polymer-lean phase, which resulted from the slower solidification of PVDF.¹⁸ At polymer concentration of 70 wt %, smaller and more uniform spherulitic particles were found in the cross-section of PVDF membrane quenched at lower temperature, because low quenching temperature was in favor of nucleation but does not favor the growth of crystalline nucleus.⁶

Porosity and tensile strength

The porosity and tensile strength of microporous PVDF membranes obtained by quenching PVDF/DPC solutions at different PVDF concentrations into ice water are shown in Figure 6. As shown in Figure 6, with an increase in the polymer concentration from 20 to 70 wt %, the tensile strength increased from 2.10 to 13.72 MPa; however, the porosity decreased from 78 to 18% gradually. As mentioned earlier, for the solution with higher PVDF concentration, the mean pore size of the resulting membrane was relatively small and the porosity was lower. In addition, it was easier for PVDF segments to be interconnected at higher polymer concentration.¹⁰ Therefore, the tensile strength of PVDF membrane increased with increase in the PVDF concentration.

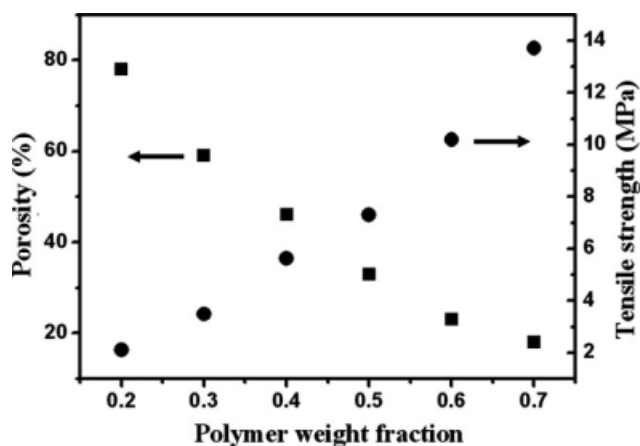


Figure 6 Porosity and tensile strength of PVDF membranes prepared by quenching PVDF/DPC solution into ice water.

CONCLUSIONS

In the phase diagram for PVDF/DPC system, the monotectic point was extended to a high polymer concentration of approximately 56 wt %. However, PVDF could not form homogeneous blends with DPM below the boiling temperature of DPM. These phenomena could be explained by different compatibilities between polymer and diluents.

The polymer concentrations were chosen at different positions of phase diagram to control the mechanism of phase separation, and so the kinds of pore structure including bicontinuous, cellular, and compact spherulitic structures could be obtained by changing polymer concentration of PVDF/DPC solutions. In addition, with an increase in polymer concentration from 20 to 70 wt %, the tensile strength of the resulting membranes increased from 2.10 to 13.72 MPa; however, the porosity decreased from 78 to 18%. The quenching temperature could effectively influence the growth rate of polymer-lean phase at a

low polymer concentration and the growth rate of spherulite at a high polymer concentration. When quenching the PVDF/DPC system in water at lower temperature, smaller pore sizes and spherulitic particles were obtained at polymer concentration of 30 and 70 wt %, respectively.

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